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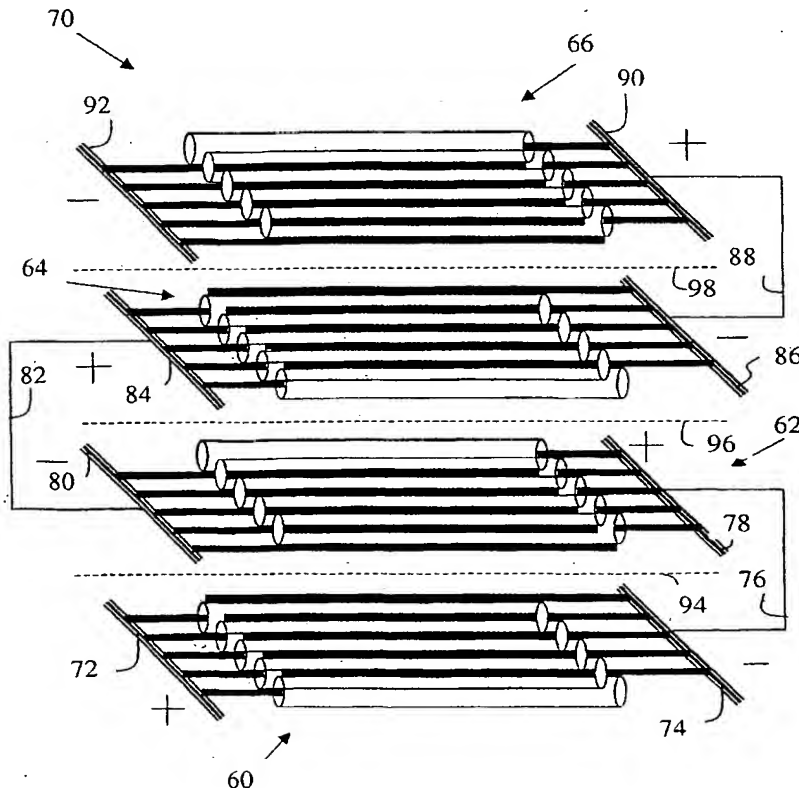
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- (22) International Filing Date: 23 July 2001 (23.07.2001) (74) Agent: HULTQUIST, Steven, J.; Intellectual Property/Technology Law, P O Box 14329, Research Triangle Park, NC 27709 (US).
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(54) Title: MICROCELL ELECTROCHEMICAL DEVICES AND ASSEMBLIES, AND METHOD OF MAKING AND USING THE SAME



(57) Abstract: Microcell structures and assemblies are efficiently utilized for electrochemical generation/conversion of energy. The microcell structures of the invention are readily constructed from discrete fibrous microcell elements that are fabricated in sheet form (60, 62, 64, 66) and assembled into layered, sub-bundled and bundled conformations that produce high voltage, high power density outputs in applications such as fuel cell and battery systems.

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# MICROCELL ELECTROCHEMICAL DEVICES AND ASSEMBLIES, AND METHOD OF MAKING AND USING THE SAME

## DESCRIPTION

### Field of the Invention

This invention relates to microcell electrochemical devices and assemblies, methods of making same by various techniques, and use of such devices and assemblies.

### Description of the Art

In the field of energy supplies and energy conversion devices, and particularly in the development of fuel cells and batteries, there has been continuing effort to develop devices with significant power outputs (high current and/or high voltage), high power density, and high energy output per unit volume.

Structurally, electrochemical cells such as batteries and fuel cells are relatively simple, utilizing respective positive and negative electrodes separated in such manner as to avoid internal short circuiting, and with the electrodes being arranged in contact with an electrolyte medium. By chemical reaction at the electrodes, the chemical energy of the reaction is converted into electrical energy with the flow of electrons providing power when the electrode circuit is coupled with an external load.

Battery cells may use separator plates between respective electrodes so that multiple sheet elements are arranged in successive face-to-face assemblies, and/or such sheets may be wound together in a (spiral) roll configuration.

The fuel cell is of significant current interest as a source of power for electrically powered vehicles, as well in distributed power generation applications.

In fuel cells, a fuel is introduced to contact with an electrode (anode) and oxidant is contacted with the other electrode (cathode) to establish a flow of positive and negative ions and generate a flow of electrons when an external load is coupled to the cell. The current output is controlled by a number of factors, including the catalyst (e.g., platinum in the case of hydrogen fuel cells) that is impregnated in the electrodes, as well as the kinetics of the particular fuel/oxidant electrochemical reaction.

Currently, single cell voltages for most fuel cells are in the range of about 0.6-0.8 volts. The operating voltage depends on the current; as current density increases, the voltage and cell efficiency correspondingly decline. At higher current densities, significant potential energy is converted to heat, thereby reducing the electrical energy of the cell.

Fuel cells also may be integrated with reformers, to provide an arrangement in which the reformer generates fuel such as hydrogen from natural gas, methanol or other feed stocks. The resulting fuel product from the reformer then is used in the fuel cell to generate electrical energy.

Numerous types of fuel cells have been described in the art. These include:

polymer electrolyte fuel cells, in which the electrolyte is a fluorinated sulfonic acid polymer or similar polymeric material;



alkaline fuel cells, using an electrolyte such as potassium hydroxide, in which the KOH electrolyte is retained in a matrix between electrodes including catalysts such as nickel, silver, metal oxide, spinel or noble metal;

phosphoric acid fuel cells using concentrated phosphoric acid as the electrolyte in high temperature operation;

molten salt fuel cells employing an electrolyte of alkali carbonates or sodium/potassium, in a ceramic matrix of lithium aluminate, operating at temperatures on the order of 600-700 degrees C, with the alkali electrolyte forming a high conductive molten salt;

solid oxide fuel cells utilizing metal oxides such as yttria-stabilized zirconia as the electrolyte and operating at high temperature to facilitate ionic conduction of oxygen between a cobalt-zirconia or nickel-zirconia anode, and a strontium-doped lanthanum manganate cathode.

Fuel cells exhibit relatively high efficiency and produce only low levels of gaseous/solid emissions. As a result of these characteristics, there is great current interest in them as energy conversion devices. Conventional fuel cell plants have efficiencies typically in the range of 40-55 percent based on the lower heating value (LHV) of the fuel that is used.

In addition to low environmental emissions, fuel cells operate at constant temperature, and heat from the electrochemical reaction is available for cogeneration applications, to increase overall efficiency. The efficiency of a fuel cell is substantially size-independent, and fuel cell designs thus are scalable over a wide range of electrical outputs, ranging from watts to megawatts.

A recent innovation in the electrochemical energy field is the development of microcells - small-sized electrochemical cells for battery, fuel cell and other electrochemical device applications. The microcell technology is described in U.S. Patent Nos. 5,916,514; 5,928,808; 5,989,300; and 6,004,691, all to Ray R. Eshraghi. The microcell structure described in these patents comprises hollow fiber structures with which electrochemical cell components are associated.

The aforementioned Eshraghi patents describe an electrochemical cell structure in which the single cell is formed of a fiber containing an electrode or active material thereof, a porous membrane separator, electrolyte and a second electrode or active material thereof. Cell designs are described in the Eshraghi patents in which adjacent single fibers are utilized, one containing an electrode or active material thereof, the separator and electrolyte, with the second fiber comprising a second electrode, whereby the adjacent fibers constitute positive and negative electrodes of a cell.

The present invention embodies additional advances in the Eshraghi microcell technology.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figures 1-4 are perspective views of fibrous element structures illustrating the fabrication of a microcell assembly.

Figure 5 is a perspective view of a connector for joining current collector or electrode elements of a microcell fiber assembly.

Figure 6 is a microcell assembly according to one embodiment of the invention, with a terminal at one end of the assembly.

Figure 7 is an exploded perspective view of a microcell assembly showing series-connected microcell sheets.

Figure 8 is a schematic view of a layered arrangement of microcell sheets, joined in series relationship.

Figure 9 is a 3-dimensional perspective view of a series-connected arrangement of microcell layers.

Figure 10 shows a potted arrangement of microcell sheets.

Figure 11 is a perspective view of a duct that is perforated on the top surface, and optionally on the bottom surface for the fabrication of double stack bundles of electrochemical cells.

Figure 12 is a cross-sectional elevation view of a microcell fiber bundle potted in a vessel.

Figure 13 is a side elevation view of the vessel of Figure 12.

Figure 14 is an elevational cross-sectional view of a double stack of microcell sheets.

Figure 15 is a side elevation view of a double stack of microcell devices arranged in sheets, comprising a stack on each side of a perforated duct.

Figure 16 is a perspective view of potted fibers on one side of a perforated feed duct.

Figure 17 shows a vessel with fibers laid on both sides of the perforated feed duct.

Figure 18 is a side elevation view of an electrochemical cell device comprising an assembly of microcells.

Figure 19 shows a perforated feed tube used as a mandrel in forming microcell structures.

Figure 20 shows fibrous microcell and shell side current collector sheets that can be rolled or wound around the perforated tube of Figure 19, with the sheets being shown during rolling in Figure 21 and as finally rolled into shape in Figure 22.

Figure 23 shows sheets of fibrous microcell elements and shell side current collectors, and an insulating sheet (e.g., of fiberglass or porous plastic material).

Figure 24 is a perspective view of a sheet assembly including two sheets of fibrous microcell elements and shell side current collectors.

Figure 25 is a side elevation view of a microcell assembly with off-set fiber layer sheets.

Figure 26 is a cross-sectional view of a microcell bundle.

Figure 27 is a side elevation view of series-connected microcell sub-bundles according to one embodiment of the invention.

Figure 28 is a perspective view of a connector that may be used to join component microcell sub-bundles in series.

Figure 29 is a cross-sectional elevation view of a multibundle assembly, wherein each bundle has a corresponding feed tube associated therewith.

Figure 30 is a cross-sectional elevation view of a multibundle assembly, wherein the respective bundles are connected in series.

Figure 31 is a cross-sectional view of a fuel cell module with multiple sub-bundles wherein blank seal elements provide closure members for the face sheet of the module enclosure.

Figure 32 is a side view of a fuel cell module with multiple sub-bundles of microcell elements, with a feed tube in a manifolded arrangement.

Figure 33 is a side elevation view in section, showing penetration of a feed tube into the interior volume of the housing of a module containing microcell sub-bundles according to one embodiment of the present invention.

Figure 34 is a cross-sectional view of a microcell assembly in which heat exchange fibers or tubes are provided in interspersed relationship to the microcell bundles.

Figure 35 is a cross-sectional elevation view of a fuel cell module, showing air/fuel passages and heat exchange passages, interspersed between the sub-bundles.

Figure 36 is a cross-sectional view of a microcell bundle wherein hollow fibers function as outer electrode elements and enable heat exchange.

Figure 37 is a side elevation in cross section of a fuel cell with heat exchange/current collector hollow fibers.

Figure 38 is a cross-sectional elevation view of a fuel cell module with heat exchange from current collectors by means of conduction.

Figure 39 is a schematic depiction of a fuel cell system, according to one embodiment of the invention.

Figure 40 is a cross-sectional view of a double membrane design with an electrically conductive perm-selective membrane on the anode or cathode element of the microcell.

Figure 41 is a cross-sectional view of a double separator design with perm-selective membranes protecting the anode or cathode elements of the microcell.

Figure 42 is a cross-sectional view of a double separator design with perm-selective membranes covering both anode and cathode elements of the microcell.

Figure 43 is a cross-sectional view of a double separator design with perm-selective membranes covering both anode and cathode elements of the microcell and with a porous, electrically conductive inner separator.

Figure 44 is a cross-sectional view of a double separator design with perm-selective membranes covering both anode and cathode elements of the microcell and with reformer catalyst on the inner wall of the inner separator.

Figure 45 is a schematic flowsheet of a solution impregnation system for impregnation of a membrane fiber with Nafion or electrocatalyst.

Figure 46 is an elevation view of a metallic fiber having a polymeric compound on its outer surface.

Figure 47 shows the corresponding fiber of Figure 46 after pyrolysis, with a pyrolyzed carbon coating on the outside surface thereof.

Figure 48 shows a fibrous carbon current collector laid along a coated metallic fiber.

Figure 49 shows the fiber assembly of Figure 48 after a disconnection break of the coated metallic fiber.

Figure 50 shows a cross-section of a hollow fiber and microcell tube bundle, in which the plane hollow fiber elements are used for channeling water from the assembly.

Figure 51 shows a vertically upward extending bundle of microcells, arranged so that water from the module drains to a lower plenum space for removal.

**DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED  
EMBODIMENTS THEREOF**

The disclosures of Eshraghi U.S. Patent Nos. 5,916,514; 5,928,808; 5,989,300; and 6,004,691 hereby are incorporated herein by reference, in their respective entireties.

As used herein, the term microcell refers to an electrochemical cell energy generation or conversion structure, including a porous membrane separator having electrolyte disposed in porosity thereof. The porous membrane separator is in contact with electrically conductive fibers that in turn are in contact with or are coated with electrocatalyst forming positive and negative electrodes for the electrochemical cell.

While the ensuing description herein is primarily directed to fuel cell embodiments of the instant invention, it will be appreciated that the description can be analogously applied to corresponding battery cells and to other forms of electrochemical cell devices, consistent with the invention.

A battery cell of course differs from a fuel cell in that the (electrode) active material in a battery is present and stored in the cell, as opposed to being externally furnished to the structure when electrochemical activity is desired.

Accordingly, when used in a battery cell, the microcell does not require a lumen at the center of the fiber, thereby correspondingly simplifying the bundling of fibers in modular assemblies for battery cell applications. Microcells for battery cell applications thus have structural and operational differences from microcells used in fuel cells.



In a specific form, the microcell comprises an inner electrode active material, a microporous membrane separator in contact with the inner electrode active element, electrolyte in pores of the microporous membrane separator, and an outer electrode active element, wherein each of the inner and outer electrode active elements comprises at least one of electrode, current collector and electrocatalyst components.

In another specific form, the microcell may include a fibrous, inner electrode that is encapsulated by a microporous membrane separator with an electrolyte disposed in porosity of the microporous membrane separator, and with electrocatalyst impregnated or coated on the bore or shell side of the fiber (to form an inner or outer electrode, respectively) along with electrically conductive material.

In fuel cell applications, the bore of the microcell hollow fiber defines a lumen for passage therethrough of gaseous or liquid feed (e.g., fuel or oxidant) components. A wide variety of electrolyte types can be used in the microcell fuel cell, depending on the specific application involved.

In a preferred form, all components of the microcell are fabricated in a single fiber assembly. The microcells can be of any predetermined length, typically with a length to diameter ratio significantly greater than 1, and are readily formed into microcell assemblies, including bundled forms as hereinafter described in greater detail. Such microcell assemblies, or collections of such assemblies, may be aggregated to form a fuel cell module, similar in overall arrangement to a shell and tube heat exchanger.

When the microcell elements are fabricated into bundled multi-cell modules in a unitary overall construction, the resulting compact unitary configuration provides high density energy output and

enables minimization of the volume (and "footprint") of the fuel cell or other electrochemical cell apparatus fabricated from such bundles.

The microcell apparatus of the invention in one embodiment is fabricated with the inner electrode (or a multiplicity of current collector fibers) being encapsulated by a microporous membrane separator. The electrocatalyst of the inner electrode in such embodiment is coated or impregnated on the inner wall of the membrane separator (or coated on the inner current collector fibers).

The electrocatalyst in one embodiment is impregnated onto the membrane separator wall from a catalyst solution. In another, alternative embodiment, a thin ink formulation of the catalyst is pumped through the bore of the membrane separator during the membrane spinning process.

One technique of forming porous separator membrane-electrode assemblies involves coating current collector fibers with an electrocatalyst formulation. Such coating in one embodiment is carried out in an extrusion process. In another embodiment, the current collector fibers are coated from a plating solution. In yet another embodiment, the current collector fibers are coated by plasma deposition of a metal catalyst.

In forming a fuel cell stack or module, the microcell fibers are bundled and potted in order to isolate and seal the bore side and the shell side of the cells. For large fuel cell structures, microcells may be bundled around a perforated mandrel, such that the mandrel becomes the gas input structure for the shell side of the cells.

With respect to the microporous membrane separator element as used in fuel cell embodiments and in other electrochemical cell embodiments of the present invention, any suitable means and method for

electrolyte impregnation or incorporation are usefully employed. An illustrative and preferred technique for impregnation of the electrolyte is solution impregnation.

The porous membrane separator element itself can be of widely varying type and structure, and formed for a specific type of fuel cell or other electrochemical cell application. For polymer electrolyte fuel cells, for example, an asymmetric channelized porous structure is preferred to provide a contiguous phase of the ion exchange polymer adjacent to the electrocatalyst layer. For acid or alkaline fuel cells, a foam-like structure of the porous membrane element is desirable. The choice of membrane separator conformation and morphology is readily determinable without undue experimentation, as will be appreciated by those skilled in the art.

Fuel cells formed from microcells in accordance with a preferred aspect of the invention are monopolar and do not require bipolar flow field plates. Since the cells and current collectors are in fiber form, a high level of electrode surface area can be compacted in very small volumes. In parallel connection of individual bundled cells, wherein current is additive, very high current density per unit volume is achievable, allowing the microcell assembly to operate at high voltage and high efficiency.

In one embodiment, inner electrodes of respective microcells are connected to form a first terminal of a microcell assembly, and current collectors on the outer shell of the fiber elements or on the outer shell of a bundle of such microcells, forms a second terminal. When such assembly is constructed and arranged for fuel cell usage, fuel and oxidant are passed over electrodes on the corresponding respective shell and bore sides of the bundle. In the individual microcell elements of this fuel cell, the microporous membrane is impregnated with an appropriate electrolyte and forms a barrier or separator element. Depending on the electrolyte type, the microporous matrix and electrolyte can combine to form a new structure in the form of a solid matrix or a liquid-solid matrix.

In fuel cell applications utilizing microcell devices containing a single fiber inner electrode element, the size of the inner electrode element is selected to provide an appropriately dimensioned lumen on the bore side of the membrane separator containing the electrode. Multiple fibers can also be positioned in the bore of a hollow fiber membrane separator to provide interstitial space forming a lumen in the hollow fiber. The formation of the lumen is important since the lumen allows (liquid or gaseous) fuel or oxidant to reach the inner electrode in the operation of the fuel cell.

In a preferred form, an electrocatalyst and the electrically conductive material of a second electrode is coated, extruded or impregnated on the outer shell of the microporous membrane separator and electrolyte is disposed in the micropores of the membrane separator, to complete the microcell structure.

The microporous membrane separator may be formed of any suitable material of construction. In one embodiment, the microporous membrane separator is fabricated from a material selected from the group consisting of semi-permeable, ion-exchange membranes, and a porous membrane coated on a shell or bore side thereof with a perm-selective or an ion-exchange polymer.

In the microcell structure, the inner electrode or current collector is retained in a tightly-held manner in the bore of the separator and is contiguous to the inner wall of the fiber, for interfacial contact with the electrolyte or electrolyte/electrocatalyst layer. The outer electrode or current collector also makes intimate contact with the shell side electrolyte, or with the electrolyte/electrocatalyst layer of adjacent cells, when the fibrous microcell structures are densely bundled with one another.

Accordingly, the lumen of the microcell structure in fuel cell applications must be sufficiently "open" to allow passage of the gaseous feed (fuel or oxidant) through the lumen during normal operation. For such purpose, the fuel cell apparatus desirably includes a pump, fan, blower, compressor, eductor, or the like. Since the flow rates required for fuel cell operation entail relatively low pressure differentials, pumping requirements (for gaseous feed flow through the lumen of the microcell hollow fiber) are readily accommodated by commercially available fluid driver devices of the above-mentioned types.

### **Series Connection of Microcell Structures and Assemblies**

To achieve high current density at a single microcell voltage level, a number of microcells are connected together in parallel. Parallel connection of microcells for such purpose is readily effected by bundling the microcells in parallel relationship to one another and connecting the end portions of the current collectors at each extremity of the resulting microcell assembly.

In order to achieve high voltages, however, above the voltage afforded by a single microcell, it is necessary to connect microcells in series with one another. As described more fully hereinafter, various methods may be employed to effect series connection, depending on the geometry of the microcell assembly that is desired. For example, a rectangular configuration or a cylindrical configuration may be desired.

In accordance with the invention, a sub-bundle of parallel fibrous microcells is first constructed to obtain the desired current. The sub-bundles then are connected in series to achieve a desired voltage.

One preferred approach to forming a sub-bundle microcell assembly is to form a sheet arrangement of generally parallelly aligned microcell elements, wherein the microcells are in side-by-side relationship to one another, with the current collectors extending from one end of the generally planer sheet, in side-by-side register with one another (i.e., so that the current collector ends are generally arranged in a single plane with respect to one another, or otherwise so that the current collectors protruding from the microcells are generally coextensive in length relative to the face of the microcell sheet assembly from which they protrude). Next, the first layer of microcell elements is overlaid by a second layer comprising outer current collector elements, arranged so that the outer current collectors extend from an opposite side of the superimposed sheet from that from which the inner current collectors protrude. The outer current collectors likewise extend outwardly to a generally same length, so that the ends of the outer current collectors are in register with one another, residing generally in a single vertical plane relative to a flat, horizontal plane of the sheet assembly.

For purpose of forming the above-described sheet assembly, the constituent fibrous microcell elements in the first layer may be secured to one another to provide a unitary web or sheet form of such elements. In like manner, the outer current collectors overlaid on the fibrous microcell elements may be secured to one another to a sheet or web confirmation, such as by an inner connecting mesh or woven structure, transversely laid strips of adhesive tape, or other means by which a parallel assembly of current collector elements is provided.

It will be appreciated that any suitable means and methods may be employed to form the respective sheet-like layers of the microcell assembly just described. Such layers can be pre-formed, for example, by weaving the microcell or current collector fibers into sheets or embedding them in a resinous matrix, or in any other suitable manner.

Once the layer of microcell elements and the layer of outer current collector elements is contacted in superimposed relationship with one another, the composite structure then can be rolled into a cylindrical shape and potted at each of respective opposite ends, to form a sub-bundle assembly comprising a multiplicity of microcells.

Potting of such assembly can be carried out in any suitable manner, using methods conventionally employed to pot hollow fiber membranes, e.g., in the fabrication of hollow fiber filtration modules. Each resultant potted sub-bundle thereby has a positive and negative terminal at each end, with one such terminal being formed by the inner current collector elements protruding from the microcell elements of the first-described layer, and the other terminal being formed by the outer current collector elements protruding from the opposite end of the sub-bundle.

Sub-bundles then are connected in series by connecting the positive terminal of a first sub-bundle to a negative terminal of a next sub-bundle, and so on in consecutive fashion. The resulting long strand of connected sub-bundles then is re-bundled into a cylindrical shape, by folding each bundle in an alternating fashion at each end and at the connection between each succeeding microcell. The resulting assembly of sub-bundles folded into parallel arrangement with one another then is potted again at each end thereof to form a bundle as a composite structure comprising a multiplicity of sub-bundles.

The bundle in consequence contains fibrous microcells in both parallel and series connection, constituted in a unitary structure that may then be placed in a casing in the manner of a shell and tube heat exchange assembly, as hereinafter described in greater detail.

It is evident from the foregoing discussion that the avoidance of short-circuiting between sub-bundles requires that each sub-bundle be covered or encased with a porous yet electrically insulating material. Accordingly, each sub-bundle may be sheathed or sleeved in a fiberglass or polymeric material encasement member, in to which the sub-bundle may be inserted or about which the encasement material may be wrapped.

Sub-bundles alternatively may be formed and the packed into a bundle by alternating each end so that a positive terminal end of a sub-bundle is in proximity to a negative terminal of another sub-bundle. The sub-bundles in this alternative technique can first be potted and then connected in series, by connection of the positive terminal of a first sub-bundle to a negative terminal of a next adjacent sub-bundle. The sub-bundles may be connected simply by making an electrical connection between each microcell. Alternatively, an end plate having a mirror image of the location of sub-bundle connection nodes (where all the microcell fibers are connected in parallel in a sub-bundle) on its face, and an imprint of series connections of the terminals designed and built into the plate may be employed, so that electrical connection of the plate with each node of the bundle will automatically yield a series connection.

As yet another alternative to sub-bundle potting, each sub-bundle may be fabricated with a sealed tube sheet member at each end. Each sub-bundle then can be inserted into a casing having openings at each end thereof that are the same size as the parameter (outer circumference) of the sub-bundle. In such fabrication, each sub-bundle may be sealed at each respective end of the housing, e.g., with O-ring seals or other sealing means, without the requirement of having to pot the sub-bundles again. In such configuration, each sub-bundle can be removed from or introduced to the housing in a simple and readily affected manner, allowing for increase or reduction in power generation capacity of the overall microcell apparatus.



Alternatively, a sub-bundle article can be fabricated in a rectangular confirmation by placing layers of microcells and outer current collectors over each other in alternating and repeating sequence to achieve a desired height and rectangular cross-section. The constituent layers of microcell fibrous elements and outer current collectors can be preformed in sheet-like form, as previously described.

In forming a series connection of sub-layers of respective fibrous microcell elements and outer current collectors in the respective layers, the current collector elements are generally of similar length characteristics to the fibrous microcell elements, such that respective fibrous microcell element and outer current collector layers are longitudinally off-set in relation to one another. In such arrangement, the outer current collector elements are longitudinally displaced beyond one end of the fibrous microcell element layer, and is correspondingly shorter at the opposite end so that the first layer (underlying layer) of fibrous microcell elements extends beyond the ends of the layer of outer current collectors.

Thus, at each end of the layered assembly, there is a line of "short ends" of the upper or lower layer, and it is at this short end that the potting member is formed at each of the ends of the overall assembly.

On this sub-layer assembly a layer of porous, electrically insulating sheet material is placed, and a second sub-layer assembly then is formed on the porous, electrically insulating sheet. In the second sub-layer assembly, a bottom layer is placed directly on the porous, electrically insulating sheet and overlaid with a layer of outer current collectors, off-set from one another, and arranged such that the positive terminal of the new sub-layer is on the same side of the overall assembly as the negative terminal of the first sub-layer. This pattern of fabrication is continued until a desired sub-layer height is reached and a desired voltage is achieved. The ends of the respective positive and negative current

collectors from each end are then connected to each other with, for example, an electrically conductive rod or strip member, as hereinafter described.

Alternatively, the layered assembly may be fabricated, with electrical connection of the fiber sheets with positive and negative ends from adjoining sub-layers initially, prior to stacking of the respective sub-layers. A final stack of sub-layers is then potted at both ends of the assembly, to isolate and seal the bore of the sub-layer assembly from the shell side. The potted bundle of the fiber stack then can be placed on a perforated duct that will function as a feed inlet to the shell side of the hollow fibers in the assembly. The fibrous microcell elements and the outer current collectors can alternatively be potted as the fibers are being layered, e.g., by depositing a line or bead of epoxy or other potting compound at both ends as the respective layers are being laid. The viscosity of the potting material is suitably chosen so that complete wetting of the fibrous microcell elements takes place, to ensure leak-tightness of the resultant tube sheet.

Once potted, the bundle or stack of microcell layers is placed in a housing such that the shell and bore of the microcell elements are sealed and isolated when a feed is introduced on either side (shell side or bore side). The resulting unit has the configuration of a rectangular shell and tube heat exchanger, and such unit is advantageously fabricated with at least one inlet to the housing for introducing feed to the bore side and at least one outlet in the housing for removing depleted feed from the bore side.

When the microcell elements are provided in a stack of layers, such stack is placed on a duct perforated between the potting members at respective ends. A non-perforated section of the duct extends through one end of the housing, e.g., with the feed inlet or outlet on the bore side of the microcell elements, as described, and with the duct extending sealingly through the housing to provide a feed inlet to the shell side of the microcell elements. The layered microcell stacks may be placed on

both sides of a perforated feed duct to form a symmetric double stack, as hereinafter described in greater detail.

In accordance with one aspect of the present invention, small sub-bundles of microcell assemblies can be electrically connected in series in the same cell housing, or smaller fuel cell modules can be electrically connected in series to increase the overall cell voltage. One approach for achieving high voltage levels, in accordance with another embodiment of the present invention, is to manifold fuel cell stacks (each comprising a plurality of microcell devices) to gas feeds in a parallel fashion, with the stacks themselves being series-connected assemblies of microcell bundles.

In one embodiment, electrically conductive fibers are bundled with microcell devices, so that the electrically conductive fibers function as current collectors on the shell side of the fibers. The shell side current collectors, or alternatively the outer electrodes coated with suitable electrocatalyst, are connected to a common plate to constitute a first terminal for the bundled assembly. Correspondingly, inner electrodes extending through the bore of the microcell fibers are connected to a plate forming a second terminal for the assembly.

In such fuel cell assembly, fuel or oxidant is passed over the electrodes on the corresponding respective bore or shell side of the fibers, and the electrolyte-incorporating membrane separator prevents migration of the fuel or oxidant to the other electrode.

In accordance with the invention, the microcell fiber structures are usefully potted to form sub-bundles of a larger ultimate bundled structure, with the sub-bundles being connected in series or parallel (or, as discussed hereinafter, some structures or sub-bundles can be parallel connected, with the parallel-connected assembly of microcell elements then being series-connected to other sub-bundles; the

converse arrangement, wherein series-connected microcell elements form sub-bundles that are parallel-connected to one another, also is usefully employed in some applications).

In one preferred embodiment, sub-bundles of the microcell fiber structures are fabricated, and then the sub-bundles are aggregated with other sub-bundles, and potted again to form the fuel cell module. The potting medium advantageously used for such structural fixation of the microcell fiber structures or sub-bundles is any suitable potting or encapsulant medium, such as epoxy, urethane, silicone, EPDM rubber, or other encapsulant media.

The sub-bundles can be made with tube sheets at each end with O-ring seals, similar to the process employed in the final module assembly, and with the sub-bundles then inserted in a metal or polymeric sheet material having holes formed in it. The fuel cell casing then will have two faces, one at each end, with holes cut into it the size of the outer diameter of the sub-bundled tube sheet.

By this arrangement, sub-bundles can be added to or removed from the overall module to increase or decrease power (e.g., in a power source for stationary application, or alternatively for motive transport applications such as electrical vehicles, to provide adjustable vehicle power). The holes in the faces can be sealed with blank sheets of the same size as the holes, if sub-bundles are removed from the module. This feature also provides capability for servicing individual sub-bundles, by removing defective sub-bundles and replacing them with new sub-bundles. The sub-bundles can themselves be potted units comprising smaller sub-bundles.

Figures 1-4 are perspective views of fibrous element structures illustrating the fabrication of a microcell assembly.

As shown in Figure 1, a fibrous microcell element sheet 10 is formed of a plurality of fibrous microcell elements 12, laid side by side one another in parallel alignment. The respective fibrous microcell elements 12 can be consolidated by a plurality of sewn seams 16 as shown, or by use of tape, adhesive bonding or other method of affixation to produce a unitary fibrous microcell element sheet.

The sheet 10 as illustrated is aligned with first ends 18 of the elements 12 being in transverse register with one another, i.e., the ends are generally coextensive in axial extent with one another, so that the ends 18 lie in a common vertical plane extending across the face of the sheet from which the internal current collectors 14 protrude.

In like manner, the opposite ends 20 of the fibrous microcell elements 12 are in transverse register with one another, with the ends generally aligned with one another in a transversely extending vertical plane at the opposite face of the fibrous microcell elements 12.

In this manner, the fibers are laid flat adjacent to one another and consolidated in a web structure, to form a sheet of fibers.

A plurality of external current collectors 24 are likewise secured together in parallelly aligned side by side arrangement, by a sewn seam 26, or alternatively, a tape, glue strip, or other consolidating means, to form a sheet 22 as shown in Figure 2. In such sheet 22, the respective ends 28 and 30 of the constituent current collectors 24 are in register with one another so that all ends of the fibrous current collectors at each extremity of the web lie in a transversely extending vertical plane at such extremity.

Next, the sheet 10 of fibrous microcell elements 12 and the sheet 22 of fibrous current collector elements 24 are stacked, with the current collector sheet 22 on top of the fibrous microcell elements sheet 10, to form a conjoint structure 32 as shown in Figure 3.

In such conjoint structure 32, the respective sheets 10 and 22 are longitudinally off-set with respect to one another, so that the internal current collector elements 14 of sheet 10 extend beyond the ends of the external current collectors of sheet 22 as shown, and with the external current collectors of sheet 22 correspondingly extending beyond the ends of the internal current collectors 14 of sheet 10 at the opposite end of the conjoint structure. The respective external current collectors of the overlying sheet 22 thus are in contact with associated fibrous microcell elements in the underlying sheet 10.

In Figure 4, the conjoint structure 32 of Figure 3 is a bottom layer of an assembly that is formed by overlying the bottom layer with a second layer 36 including a parallelly aligned arrangement of fibrous microcell elements 38 forming a corresponding sheet, and overlaid in the second layer by a sheet including external current collectors 48 secured together by a sewn seam 40 as shown.

In the second layer, the fibrous microcell elements 38 are in register with one another at their respective ends 42 and 44, and the sheet of external current collectors 48 is longitudinally displaced from the sheet of fibrous microcell elements 38. By such arrangement, the external current collectors 48 extend beyond the ends 42 of the fibrous microcell elements 38, and the internal current collectors 46 of the fibrous microcell elements 38 extend beyond the ends of the external current collectors 48.

Concurrently, the longitudinally protruding current collectors from the respective first and second layers at each of the ends of the assembly are coextensive in axial extent with one another. A porous

insulating layer of polymeric or fiberglass sheet 50 is placed between the layers 32 and 36, as shown in Figure 4.

Figure 5 is a perspective view of a connector 52 for joining current collector or electrode elements of a microcell fiber assembly. The connector 52 has two leaves 54 and 56 that are at a 90° angle in relation to one another, with the leaves being crimpable toward one another. When a group of current collector or electrode elements is placed between the leaves of the connector and the leaves are crimped together, the current collector or electrode elements then are secured in electrical contact with one another.

Figure 6 shows the microcell assembly of Figure 4, with the current collector elements at the right-hand portion of the drawing shown as being secured to the connector 52 so that the current collector elements are coupled in electrical contact with one another.

Figure 7 is an exploded perspective view of a microcell assembly 70 showing series connected microcell sheet layers 60, 62, 64 and 66. The bottom sheet layer 60 comprises internal current collector elements that are connected by connector 72, and the overlying sheet of external current collectors in such layer are in turn joined to connector 74.

The next upper layer in the assembly includes internal current collectors connected by connector 78, which is joined by interconnect 76 to connector 74, as well as external current collectors joined to connector 80.

Connector 80 is joined by interconnect 82 to connector 84 of the next upper layer in the assembly.

Connector 84 connects the internal current collectors of such next upper layer, and the connector 86 at

the opposite end of the layer connects external current collectors of the layer to the connector 90 of the top layer in the assembly via interconnect 88.

Connector 90 connects the internal current collectors of the top layer in the assembly and the external current collectors at the opposite end of the top layer of the assembly are connected by connector 92.

Each of the constituent layers in the assembly is separated from an adjacent layer by a corresponding porous insulative sheet 94, 96 and 98, respectively.

By the foregoing arrangement, each of the constituent layers in the assembly of Figure 7 is joined to a next adjacent layer in head-to-tail series relationship, as is evident from the indicated polarity of the respective connectors in the drawing.

Figure 8 is a schematic view of an assembly 100 comprising a layered arrangement of microcell layers joined in series relationship, including layers 102 and 104, separated by porous insulating sheet 110, layers 104 and 106, separated by porous insulating sheet 112, and 106 and 108, separated by porous insulating sheet 114.

Figure 9 is a three-dimensional perspective view of a series-connected arrangement 130 of microcell layers. The lowermost layer is illustrative and comprises a sheet of fibrous microcell elements 122 from which internal current collector elements 124 protrude at the left-hand side of the layer, with overlying sheet of external current collector elements 126 completing the microcell layer. The lowermost layer is shown as being electrically segregated from the next upper layer by a porous insulating layer 128, as schematically illustrated. The other layers are analogously constructed. The uppermost layer 130 as shown comprises three fibrous microcell elements arranged in side-by-side



relationship, and the other sheets of fibrous microcell elements in the assembly are correspondingly constituted. In this manner, a bundled microcell structure is formed.

Figure 10 shows a potted arrangement 136 of microcell sub-bundles 138, in which component sub-bundles are connected by series connection of their respective opposite current collector elements 140 and 142, wherein adjacent sub-bundles are separated from electrical contact and potential short-circuiting by porous, insulative sheet 147. As shown, the sub-bundles 138 are potted at their respective ends by potting members 144 and 146.

Figure 11 is a perspective view of a duct 150 that is perforated with openings 154 on the top surface 152, and optionally on the bottom surface (not shown in the view of Figure 11) for double stack bundles of the microcell layers. Two retaining walls 156, 158 are on each side, to retain the fiber sheets in position. Fibers are stacked on top of each other on the perforated duct until the desired voltage is achieved. A fluid ingress/egress conduit 160 is joined to the interior plenum chamber of the duct 150, as shown.

Fiber sheets can be potted with epoxy as they are laid. Alternatively, the fiber sheets can be bundled and potted in the vessel to finish the procedure. Fibers are potted at each end such that the open end remains open. The perforated duct will be the feed port to the shell side of the fibers.

Figure 12 shows a cross-sectional elevation view of a fiber bundle 162 potted in a vessel 150. The fiber bundle comprises layers 164 and 166 of fibrous microcell elements, with an interposed sheet 168 of external current collector elements and with a separator sheet 170 of porous insulative material between adjacent current collector and fibrous microcell element sheets. The bundle is potted by potting member 163.

Figure 13 is a side elevation view of the vessel of Figure 12, showing the retaining wall 156, and fluid ingress/egress conduit 160 of the housing, as well as the terminal connections at the respective faces 180 and 182 of the bundle.

Figure 14 shows a potted arrangement 186 of fibrous microcell element sheets, in two sub-bundles 188 and 190 on opposite sides of feed duct 196 receiving feed gas via inlet 198. The feed duct has perforations on both top and bottom surfaces, and each of the constituent sub-bundles is potted with the top sub-bundle being potted by potting member 192 and the bottom sub-bundle being potted by potting member 194.

Figure 15 shows a side elevation view of a double stack arrangement 200, comprising a stack of microcell elements on either side of the perforated duct. The gas feed 198 is shown in the drawing. The arrangement shown in this drawing includes connector/terminal elements 202, 204 and 206 connecting the corresponding current collector elements.

Figure 16 is a perspective view of an assembly 210 of potted fibrous microcell elements on one side of a perforated feed duct including gas inlet 224 and retaining wall 216. The potted rectangular bundle of microfibers is arranged with its respective ends potted by potting members 218 and 220.

Figure 17 shows a corresponding vessel 230 when fibers are laid on both sides of the perforated feed duct 238. The vessel comprises a central section 232 with an outlet 242 for discharging gas from the shell side of the microcell assembly, end section 234 featuring outlet 248 for exhausting bore-side spent gas and end section 236 with inlet 246 for introducing bore-side gas into the housing. The

perforated feed duct is arranged to introduce feed gas into the central section 232 of the housing for flow on the shell side thereof.

Figure 18 is a sectional elevation view of system 250 including a microcell bundle 280 potted at respective ends thereof by potting members 266 and 268, which are leak-tightly secured to the inner surface of the housing 252 by O-ring elements 270 and 272.

The housing 252 has a flange element 256 joining the end section 258 of the housing with the central section. The central section of the housing contains interior volume 252, which is separated from end volume 278 by potting member 268 and from end volume 282 by potting member 266. Feed inlet 276 communicates with end volume 278 and end volume 282 communicates with spent gas outlet 284.

Spent gas outlet 264 communicates with the interior volume 262. Feed tube 260 extends into the center of the microcell bundle 280 in the interior volume 262, and is perforate along its length to introduce feed gas to the shell side of the microcell bundle 280 in the interior volume, with the spent gas being discharged in outlet 264. Feed introduced into end volume 278 from inlet 276 flows through the bore side of the microcell elements in the bundle 280, and flows out of the bundle into end volume 282, following which it is discharged from the housing 252 in outlet 284.

The current collectors are joined to terminal 292 in the end volume 282, with the terminal structure extending exteriorly of the housing 252. At the opposite end volume 278, the other ones of the inner and outer current collectors are joined to terminal 290, which extends exteriorly of the housing.

Figure 19 shows a perforated feed tube 300 with open ends 302, having perforations 308 along a central part 306 of its length.

Figure 20 shows fibrous microcell and shell side current collector sheets 312, 314 that can be rolled or wound around the perforated tube 300 of Figure 19, with the sheets being shown during rolling in Figure 21 and as finally rolled into shape in Figure 22.

The sheets will be placed on top of each other such that the ends of the fibrous microcell sheet 312 extend farther than the shell side current collector sheet 314 on one side, and the shell side current collector sheet 314 extends farther on the other side. The sheets 312, 314 then are wrapped tightly around the perforated tube 300 and then potted by potting members 322 and 324.

Figure 23 shows sheets 332, 334 of fibrous microcells and shell side current collectors, and an insulating sheet 330 (e.g., of fiberglass or porous plastic material). Figure 24 is a perspective view of a sheet assembly 338, 340, 342, 344 and 346, including two sheets of fibrous microcells and shell side current collectors.

Figure 25 is a side elevation view of a microcell assembly 338, 340, 342, 344 and 346 with off-set fiber layers. The electrically insulating sheet is placed between two layers of fibers forming a cell. If the sheets on either side of the insulator are extended beyond the edge of the insulator as shown in Figure 25, then the fiber layers can be connected to one another in series.

Figure 26 is a cross-sectional view of a microcell bundle 350 comprising an assembly of positive electrodes 354 interspersed with negative electrodes 352 in a bundled conformation.

Figure 27 is a side elevation view of series-connected microcell sub-bundles 360 including sub-bundles 362, 366, 370 and 374 interconnected by connectors 364, 368 and 372, respectively. The

connectors are desirably highly flexible and most preferably omnidirectionally flexible to accommodate accordion folding of the chain of sub-bundles, so that when folded back against a preceding sub-bundle or folded forwardly against the succeeding sub-bundle.

Figure 28 is a perspective view of a connector 376 that may be used to join component microcell sub-bundles in series. The connector 376 comprises a spaced-apart pair of crimpable leaves 378, 380, each of which is crimpable by means of a pliers or similar tool, to compressively grip a protruberant group of current collectors of a sub-bundle. The leaves are electrically conductive, and are themselves interconnected by a flexible yoke element 382, which may comprise wire or metal filament, etc. that serves to electrically interconnect the respective sub-bundles with which leaves 378 and 380 are coupled.

Figure 29 is a cross-sectional elevation view of a multibundle assembly 390, wherein each bundle 391 has a corresponding feed tube 394 associated therewith, and is mounted in a tubesheet 393 and leak-tightly sealed therein with an O-ring sealant element 392.

Figure 30 is a cross-sectional elevation view of the multibundle assembly of Figure 29, wherein the respective bundles are connected in series and are numbered correspondingly to Figure 29. The respective adjacent bundles are interconnected by terminal elements 396 and 400 joined to one another by coupling wire 398 in series arrangement.

Figure 31 is a cross-sectional view of a fuel cell module with multiple sub-bundles, numbered correspondingly to Figure 29, and wherein blank seal elements 402 and 404 provide closure members for the tubesheet 393 of the module enclosure, when sub-bundles are removed.

Figure 32 is a side view of a fuel cell module 410 with multiple sub-bundles 460, 462 and 464 of microcell elements, with a feed tube 450 in a manifolded arrangement. The module includes a housing 422 enclosing a central interior volume 424 bounded by the housing wall of the module and by tubesheets 472, to which the sub-bundles are leak-tightly secured by means of O-ring elements 438, and 474, to which the sub-bundles are leak-tightly secured by means of O-ring elements 434.

The end sections of the housing enclose respective end volumes 426 and 428. The end volume 426 contains a manifold to which the feed tube 450 is joined in gas flow communication, for introduction of feed gas to each of the three sub-bundles 460, 462 and 464 by means of the manifold line 452 in communication with branch lines 454, 456 and 458 coupled to the respective sub-bundles.

The sub-bundles are joined in series relationship to one another in sequence, by connection line 440 interconnecting sub-bundles 460 and 462 and connection line 442 interconnecting sub-bundles 462 and 464. The exterior sub-bundles in such series are in turn joined respectively with terminals 444 and 446, as shown.

The right-hand end section of the housing is flangedly connected to the main central section of the housing by flange 430, with which mechanical fastener means may be coupled to leak-tightly secure the component sections of the housing to one another.

The housing is provided with a feed inlet 466 for introducing one of the fuel and oxidant streams into the end volume 426 for flow through the sub-bundles on the bore side thereof.

An outlet 468 is joined to the housing 422 at the left-hand section as shown, for discharge of spent feed gas from the end volume of the housing.

The spent gas outlet 470 is provided in the main central section of the housing, for discharge of spent feed from the shell side of the sub-bundle in the interior volume 424 of the housing.

Figure 33 is a side elevation view in section, showing penetration of a feed tube 514 into the interior volume 506 of the housing 515 of a module 480 containing microcell sub-bundles 494, 496, 489 and 498. In this arrangement, the sub-bundles are mounted in correspondingly sized receiving openings in tubesheets 500 and 502, leak-tightly secured in the housing by means of O-ring sealing elements 492. In this way, the internal volume of the housing is divided into a central volume 506 and end volumes 526 and 528.

The housing is provided with feed gas inlet 510, spent gas outlet 508 and spent gas outlet 512. Spent gas on the shell side of the sub-bundle is discharged from the housing in outlet 508, and feed gas introduced in inlet 510 is flowed through the bore side of the sub-bundle and discharged into end volume 528. From end volume 528 bore side spent gas is discharged from the housing in outlet 512.

The sub-bundles in the interior volume of housing 515 are joined in series relationship to one another by means of series connector lines 516, 518 and 520, and the outside sub-bundles in the series arrangement are in turn joined to terminals 522 and 524.

The housing 515 is openable at flange 443 to remove the right-hand end section, following which the respective sub-bundles can be accessed for repair or replacement.

Thus, microcell articles in accordance with the present invention may be readily connected in series with one another, with successive adjacent articles (fibrous microcell sheet layers, sub-bundles) being

insulated from each other by sheets or sheathing of porous insulating electrically non-conductive material, or in other manner ensuring the absence of electrical interference between such adjacent microcell articles. It will be appreciated by those skilled in the art that the numbers of sub-bundles shown in Figures 32 and 33, are illustrative only, and that the number of sub-bundles in a given application of the invention may be widely varied depending on the energy generation requirements and other structural and operational parameters of the system in specific embodiments.

In the fabrication of high voltage electrochemical cells utilizing microcell articles of the invention, a bundle or sheet-form assembly of microcells is fabricated. For example, if a design current of 200 amps is required, a number of fibrous microcell articles are connected in parallel to generate the necessary current. The resultant microcell structure then is either bundled in a cylindrical shape or used to form a multi-layered assembly. In a bundle, the positive and negative fibrous elements must be electrically insulated yet in intimate contact with each other. To achieve higher voltages, the sheets or bundles are connected in series, i.e., the positive of one cell is connected to the negative of the next adjacent cell. The cells, bundles or sheets connected in series with one another are then potted and sealed in the same housing to provide the desired high voltage electrochemical cell module.

### **Thermal Management**

When microcell elements are bundled or otherwise aggregated in a compact structural configuration to form modular electrochemical cell assemblies, the resulting electrochemical energy generation or energy conversion device generates significant heat in its operation.

Various methods can be utilized in accordance with the present invention to remove heat from the microcell assembly.



In one aspect of the invention, heat exchange tubes are distributed in the microcell bundles, sub-bundles, or other aggregated microcell assembly. In a preferred embodiment, such heat exchange tubes are aligned parallel with the fibrous microcell elements in the microcell assembly.

In another embodiment heat exchange tubes are placed between sub-bundles in the assembly, so that the heat exchange tubes extend at least from one end of a tubesheet face (in which the extremities or outer portions of the sub-bundles are mounted) to the opposite end. The number, size, and material of the heat exchange tubes are readily determined based on the amount of heat that must be recovered, the fuel cell operating temperature, the type of heat exchange fluid used, and the pumping requirement or flow rate of the fluid, as will be appreciated by those skilled in the art.

In order to maintain separation of the heat exchange fluid from the feed that is flowed to the bore side of the microcell fibers in the fuel cell module, the length of the heat exchange tubes can be selected such that the heat exchange tubes extend beyond the tube sheet that seals the bore side of the microcell hollow fibers from the shell side. The extended heat exchange tubes then are potted again to form a barrier between the bore of the heat exchange tubes and the bore of the microcell hollow fibers.

The final assembly of the fuel cell module with the heat exchange tubes preferably includes the formation of a first housing with an inlet for the introduction of heat exchange fluid in one end, a second housing between the two potted sections, i.e., the potted heat exchange tubes and the potted microcell elements, with an inlet for introduction of feed to the bore side of the microcell, and with the structure of the housing being correspondingly constructed at the opposite end, to provide corresponding respective outlets for discharge of the heat exchange fluid and the spent feed.

An alternative thermal management design for microcell electrochemical cell modules according to the present invention employs hollow, nonporous, electrically and thermally conductive tubes, as current collectors for either the bore side or the shell side or both the shell and bore side of the microcell structures. Since the current collectors terminate at opposite ends of each tube sheet, the heat exchange current collector tube will be potted as described hereinabove, to separate the heat exchange fluid housing from the bore side/feed only at one end. At the opposite end the heat exchange tube is terminated at the tube sheet.

This arrangement allows the heat exchange fluid and feed to the bore to be mixed at the outlet. In this system design the heat exchange fluid does not enter the bore of the microcell to contact the catalyst or the electrolyte. For example, the feed to the bore and the heat exchange fluid can be supplied to the module in the same direction, such that the heat exchange fluid and the feed to the bore can only mix at the feed outlet from the microcells.

The heat exchange fluid then is recovered in a separate unit, or a plenum in the housing can be provided to collect the heat exchange fluid for recycle. The separation of heat exchange fluid from the feed can be readily achieved, e.g., in the case where the feed is air or hydrogen gas.

In a specific embodiment, where the heat exchange fluid and the feed to the bore are the same (for example, air), the heat exchange fluid and the feed can be allowed to mix without further separation requirement.

In a further embodiment, heat is removed from the microcell module by conduction of heat from the current collectors on the shell side or bore side of the microcell elements. In this approach, the ends of the current collectors are extended and immersed in a heat exchange fluid in a plenum inside the

housing containing the microcell module or in a heat exchange passage located within the housing, at the feed inlet to or outlet from the fiber bores. In the latter case, the inlet and outlet of the heat exchange passage are leak-tightly segregated from the interior volume of the microcell module.

Referring to the drawings, Figure 34 is a cross-sectional view of a microcell assembly 530 in which heat exchange fibers or tubes 538 are provided in interspersed (distributed) relationship to the microcell bundles 532, as shown.

In the illustrated microcell assembly, each microcell bundle is mounted in a correspondingly sized opening in a tubesheet 536, with the microcell bundle being leak-tightly sealed in such opening by means of an O-ring sealing element. Alternatively, the microcell bundles 532 and heat exchange tubes 538 are potted to form tube sheet 536.

Figure 35 is a sectional elevation view of a fuel cell module, showing air/fuel passages and heat exchange passages thereof.

The fuel cell module 540 comprises a housing 541 in which a microcell assembly 550 is mounted, by means of potting members 552 and 554, which are circumferentially sealingly engaged with the inner wall of the housing by means of O-ring sealing elements 556 and 558. In this manner, there is formed an interior volume 560 in the housing, bounded by the potting members 552 and 554. A gas discharge outlet 586 is provided in the main central portion of the housing, in gas flow communication with the shell side of the microcell elements in the assembly 550.

The fuel cell module of Figure 35 also features respective tubesheets 562, sealingly engaged with the inner wall of the housing 541 by means of O-ring sealing element, and tubesheet 578, sealingly engaged with the inner wall of the housing by means of O-ring sealing element 580.

By such arrangement, an intermediate volume 576 is provided between the potting 552 and tubesheet 578, and an end volume is provided at the extremity of the housing, in the left-hand portion in the view shown.

Correspondingly, an intermediate volume 568 is formed between the potting member 554 and the tubesheet 562, as well as an end volume at the right-hand end portion of the housing in the view shown in Figure 35.

Coolant inlet 582 is provided at the right-hand end volume portion of the fuel cell module housing, and a coolant outlet 590 is provided at the left-hand end portion of such housing.

A feed inlet 584 is provided in communication with the intermediate volume 568 of the module and a spent feed outlet 588 is provided in flow communication with the intermediate volume 576 at the opposite end of the module.

Distributed across (transverse to the longitudinal axis) cross-section of the microcell assembly 550 is a plurality of hollow fiber heat exchange passages 604, which extend through the entire length of the microcell assembly and intermediate volumes through the tubesheets 562 and 578 into the end volumes 566 and 565, respectively.

A central feed tube 592 enters the vessel from the right-hand side thereof and extends centrally into the microcell assembly 550. Within the microcell assembly, the feed tube is of a perforate character, to provide feed to the shell side of the fibrous microcell elements in the microcell assembly.

Current collector elements in the respective intermediate volumes 568 and 576 engage respective terminals 600 and 602, which extend exteriorly of the housing 541.

The housing 541 is provided with a flange 570 connection, secured by suitable mechanical fasteners, whereby the right-hand intermediate volume and end volume portion of the housing is removable to access the interior elements of the fuel cell module.

In operation, the coolant medium (from an external source, not shown in Figure 35) is flowed into the end volume 566 and passes through the open-ended heat exchange tubes 604 and flows axially through such tubes to the opposite end volume 565, from which the coolant is discharged through outlet 590, and may for example be subjected to heat recovery for re-circulation of coolant to the inlet 582 in a continuous loop fashion. Concurrently, feed (oxidant and fuel) are introduced to respective shell side and bore side of microcell elements in the microcell assembly 550 to effect electrochemical reaction generating power transmitted to an external load through the respective terminals 600 and 602, which are joined to appropriate circuitry and external load componentry, for such purpose.

Figure 36 is a cross-sectional view of a microcell bundle 610 incorporating hollow fibers 614 interspersed with fibrous microcell elements 612. In such bundle, the hollow fibers function as outer electrode elements, as well as enabling heat exchange. Accordingly, the hollow fibers may be coated, impregnated or extruded with electrocatalyst material or otherwise configured for functional use as electrode elements, in addition to providing a throughbore passage in the lumen thereof, for flow of a

heat transfer medium, e.g., air, there through, to effect heat removal from the bundle, incident to electrochemical reaction heat generation in the operation of the microcell assembly.

Figure 37 is a side elevation in section of a fuel cell module utilizing hollow fiber heat exchange elements.

The fuel cell module 620 of Figure 37 comprises a housing 625, which is flanged with flange structure 624, to allow separation of the right-hand portion of the housing to be removed from the main central portion, to access internal structures of the module. The housing 625 contains a microcell bundle 626 which is potted by potting numbers 628 and 630, and leak-tightly sealed against the interior wall surface of the housing 625, by O-ring sealing elements 632 and 634, to define an interior volume 636 within the housing bounded by the interior walls and respective potting members 628 and 630.

In axially spaced relationship to the potting number 630 is a tubesheet 640, thereby defining an intermediate volume 660, which is sealed by O-ring element 642 against the interior wall of the housing.

The heat exchange tubes constituting current collectors, terminate at tube sheet 628, with heat exchange/current collector tubes communicating with end volume 662 of housing 622.

Exterior of the tubesheet 640 within the housing is an end volume 658.

A central feed tube 641 extends through the end-wall 622 of the housing and is centrally extended in to the microcell assembly 626. Such central feed tube is perforate within the microcell assembly, to provide fuel to the shell side of the assembly.

The right-hand portion of the housing is removable at flange 624 to provide access to the interior elements of the module.

The intermediate volume 660 is provided with an inlet 646 for introduction of fuel thereto for flow through assembly 626 to volume 662, the latter being provided with outlet 648 for discharge of spent fuel therefrom.

The intermediate volume 636 of the housing is provided with outlet 638 for discharge of shell side spent feed.

The end volume 658 of the module is provided with inlet 644 for introduction of coolant for flow through hollow fiber elements extending in to such volume, for axial flow through the hollow fiber electrode elements to the opposite end volume 662.

The hollow fiber heat exchange passages in this embodiment are formed by hollow fiber electrodes, and such electrodes are coupled in the respective end volumes to the corresponding terminals 652 and 656, as illustrated.

Figure 38 is a sectional elevation view of a fuel cell module with heat exchange from current collectors by means of conduction. The module 700 includes a housing 702 containing microcell assembly 704, potted by respective potting numbers 706, sealed by O-ring sealing element 710, and potting number 708, sealed by O-ring sealing element 712. An interior volume 720 is thereby defined, communicating with the outlet 740 for discharge of spent feed from the interior volume 720.

A central feed tube 714 extends centrally in to the microcell assembly 704 and is perforate over its length within the microcell assembly, to provide feed to the shell side of the assembly.

The end volume 724 of the housing 702 is provided with an inlet 742 for introduction of feed for flow through bore passages of the microcell assembly 704 to the end volume 722 from which spent feed can be discharged from outlets 732.

In this module, a heat exchanger 746 is contained in end volume 724 and joined in heat exchange contact with current collector elements of the microcell assembly. A heat exchange fluid (from a source not shown in Figure 38) is introduced to heat exchange or inlet 748 and circulated there through for discharge from outlet 750.

In like manner, the opposite end volume 722 contains a heat exchanger 780 with an inlet 728 receiving heat exchange fluid for flow there through and discharge from the second heat exchanger 780 through outlet 730.

The current collector elements at respective ends are joined in electrically conductive relationship to terminals 738 and 736. The left-hand portion of the housing 702 is flanged by flange 726, whereby the housing can be readily opened to access internal elements of the housing.

Figure 39 is a schematic representation of a fuel cell system, according to one embodiment of the invention.

The fuel cell system 780 includes a microcell module 782, which includes a housing 784 having joined thereto a coolant medium inlet 810, a coolant medium outlet 792, a fuel inlet 794, an oxidant



inlet 799, a spent fuel outlet 786 and a spent oxidant outlet 804. The feed outlet 786 is joined to a discharge line containing back pressure regulating valve 788 therein. In like manner, the spent oxidant outlet 804 is joined to discharge line 806 containing back pressure regulating valve 808 therein. The respective back pressure regulating valve 788 and 808 may be modulated to control the rate and extent of electrochemical reaction involving the fuel and oxidant species.

The system includes fuel supply tank 798 joined by fuel feed line 796 to the feed inlet tube 794. Correspondingly, an oxidant tank 802 is provided, joined to oxidant feed line 800 coupled to oxidant inlet 799.

The system involves a coolant recirculation arrangement, including recirculation line 816 joined to coolant outlet 792 and having disposed therein a pump 818 and heat exchanger 820. Heat exchanger 820 effects heat removal from the warmed coolant medium, so that same is recycled to the surge tank 814 for return in feed line 812 to coolant inlet 810.

Accordingly, an operation of the system shown in Figure 39, the coolant medium is flowed through hollow fiber heat exchange tubes in the housing and is continuously recirculated to the surge tank to provide a hold-up inventory of coolant for high rate electrochemical oxidation.

#### **Double Membrane Microcell Structures and Assemblies**

Microcell structures are usefully employed in specific applications of the invention in a double membrane configuration.

In one embodiment, microcell structures of such type are readily formed using an inner hollow fiber separator having an inner current collector and electrocatalyst of the inner electrode on its shell side. Such inner hollow fiber separator is encapsulated by an outer hollow fiber membrane. The pores of the outer hollow fiber membrane are impregnated with an electrolyte and the electrocatalyst of the outer electrode is coated on the shell side of the outer hollow fiber membrane, to form a double membrane microcell structure.

This double membrane microcell structure is advantageous to enable the inner hollow fiber separator to be used as a membrane to selectively allow permeation of feed (e.g., hydrogen or oxygen), as desired. This may be effected, for example, by coating the inner wall or the outer shell of the inner separator with a perm-selective material that preferentially allows the desired gas to permeate to the electrode. This double-membrane design thus is advantageous in reducing or eliminating the exposure of the electrocatalyst or the electrolyte to potential poisonous impurities in the feed. Materials that may be used in the perm-selective membrane include cellulose esters, polyimides, polysulfones and palladium.

In another microcell structure including a double membrane separator, the inner wall of the inner separator may be impregnated or coated with a CO-H<sub>2</sub>O shift low temperature reforming catalyst. In such design, the shell side of the inner separator is coated with an anode or cathode feed-selective material.

Another double membrane design involves coating both anode and cathode with a hydrogen- or oxygen-selective material. In such instance, the protective perm-selective material on the shell side of the outer hollow fiber membrane must be electrically conductive to allow electrical contact between the current collector of the outer electrode and the electrocatalyst on the shell side. A perm-selective

material such as palladium can be used for such purpose. Alternatively, an electrically conductive perm-selective material can be applied only to one of the cathode and anode components, if desired.

Yet another design utilizing double membrane fabrication employs an electrically conductive inner hollow fiber separator. Such electrically conductive hollow fiber separator may be formed of sintered metal, carbon or graphite. In some embodiments of such double membrane design, an inner current collector may not be needed depending on the electrical conductivity of the inner hollow fiber.

The inner and outer hollow fiber membrane can be of any suitable commercially available membrane material, including, for example, polypropylene, polysulfones, polyacrylonitrile, etc. In one embodiment, the membrane is treated to impart perm-selective characteristics, e.g., to selectively allow permeation of the feed gases (fuel, oxidant) while remaining impermeable to other gases and components (such as fuel impurities) that may be present. By way of specific example, a protective hydrogen-permeable barrier layer can be deposited by solution deposition, electrolytic coating, etc., to provide a film of palladium on the membrane surface that allows passage of hydrogen therethrough, but occludes nitrogen and oxygen. See, for example, Gryaznov et al., "Selectivity in Catalysis by Hydrogen-Porous Membranes," Discussions of the Faraday Society, No. 72 (1982), pp. 73-78; Gryaznov, "Hydrogen Permeable Palladium Membrane Catalysts," Platinum Metals Review, 1986, 30 (2), pp. 68-72; and Armor, "Catalysis with Permselective Inorganic Membranes," Applied Catalysis, 49 (1989), pp. 1-25.

Figure 40 is a cross-sectional view of a double membrane design of a microcell 900 with an electrically conductive perm-selective membrane on the anode or cathode element of the microcell. The microcell 900 comprises an outer electrocatalyst layer 912, the microporous membrane/electrolyte

matrix 910, electrocatalyst 908, an inner hydrogen- or oxygen-selective membrane 906, and current collector or electrode elements 902 in the inner bore 904.

Figure 41 is a cross-sectional view of a double separator design of a microcell 914 with perm-selective membranes protecting the anode or cathode elements of the microcell. The microcell 914 comprises an outer electrocatalyst layer 930, the microporous membrane/electrolyte matrix 928, electrocatalyst 926, current collector or electrode elements 922, inner porous separator 920, an inner hydrogen- or oxygen-selective membrane 918 and an inner bore 916.

Figure 42 is a cross-sectional view of a double separator design of a microcell 932 with perm-selective membranes covering both anode and cathode elements of the microcell. The microcell 932 comprises an outer hydrogen- or oxygen-selective electrically conductive membrane 948, electrocatalyst layer 946, the microporous membrane/electrolyte matrix 944 electrocatalyst 942, current collector or electrode element 940, inner porous separator 938, an inner hydrogen- or oxygen-selective membrane 936 and an inner bore 934.

Figure 43 is a cross-sectional view of a double separator design of a microcell 950 with perm-selective membranes covering both anode and cathode elements of the microcell and with an electrically conductive inner separator. The microcell 950 comprises an outer hydrogen- or oxygen-selective electrically conductive membrane 966, electrocatalyst layer 964, the microporous membrane/electrolyte matrix 962, electrocatalyst 960, electrically conductive porous current collector or electrode element 958, an inner hydrogen- or oxygen-selective membrane 956 and an inner bore 952.

Figure 44 is a cross-sectional view of a double separator design of a microcell 970 with perm-selective membranes covering both anode and cathode elements of the microcell and with reformer catalyst on the inner wall of the inner separator. The microcell 970 comprises an outer electrocatalyst layer 986, the microporous membrane/electrolyte matrix 984, electrocatalyst 982, current collector or electrode elements 980, an inner hydrogen- or oxygen-selective membrane 978, inner porous separator 976, CO water shift/reforming catalyst 974, and an inner bore 972.

#### Manufacture of Microcell Structures and Assemblies Comprising Same

For commercial high-volume production, the microcell device with most of its components desirably is fabricated in a single extrusion step, at high rate. A critical aspect of the high-volume fabrication process is encapsulating the inner electrode with the microporous membrane separator.

For such purpose, a strand or tow of electrically conductive fibers can be passed through the center of the bore former tube of an extrusion mold (spinnerette). The material that will form the backbone of the microporous membrane separator, referred to as a "dope," is extruded around the bore former tube in continuous fashion onto the strand or tow of electrically conductive fiber(s). An internal coagulant fluid, e.g., a gas such as nitrogen or a liquid such as water, is passed through the bore former tube along with the inner electrode fiber(s) or fibrous current collector(s).

In the above-described operation, the size of the microcell fiber is determined by the size of the orifice of the extrusion mold. Such orifice can be widely varied in size, e.g., from as small as 100 microns or smaller, with the membrane correspondingly being as thin as a few microns in thickness.

An electrocatalyst paste is simultaneously extruded through the bore if the method of microcell fabrication utilizes an ink paste. Extruded fiber is immersed in a quenching bath or an external coagulant medium, such as water. As the extruded fiber passes through the coagulation/quench operation, the microporous membrane structure is instantaneously formed around the inner electrode as the water-soluble pore former compound is leached out in the coagulant/quenching medium.

Pore structure, porosity and pore size of the membrane separator thereby are accurately controlled by selection and corresponding control of parameters such as the membrane dope formulation, type of coagulant used, temperature of the spinning operation, etc. Specific conditions are readily determinable for such process by simple experiment without undue effort, by those skilled in the art.

A wide variety of materials is useful to form the microporous membrane separator, including, without limitation, polysulfone, polyacrylonitrile, other high temperature polymers, glass and ceramic materials.

By the above-described spinning process, microcell articles can be fabricated at high rate on a continuous basis.

After formation of the microporous membrane separator-encapsulated inner electrode structure, such encapsulated structure is coated or impregnated on the outside (shell side) with an ion exchange polymer in the case of polymer electrolyte fuel cells, and/or electrocatalyst of the outer electrode. Such exterior coating can be advantageously performed by a similar extrusion process.

Figure 45 is a schematic flowsheet of a solution impregnation system 988 for impregnation of a membrane fiber 992 with Nafion or electrocatalyst. The membrane fiber 992 is dispensed from a fiber

spool 990 and passes, by action of the roller 994, through a solution bath 996 in which the fiber is impregnated. The impregnated fiber then passes over guide roll 998 and through the bank of heating elements 999 for final collection on take up winder 1000.

Additional applications for electrochemical cells of the invention include production of chemicals. Chemical synthesis applications are advantageously effected utilizing microcells fabricated in accordance with the invention, which provide: high current density per unit volume, as necessary for chemical synthesis; low internal resistance due to minimal electrode membrane distance (thickness); and high efficiency due to low mass transfer resistance.

In addition, microcells fabricated in accordance with the present invention may be utilized to generate hydrogen and oxygen where other forms of electric power are available. In such applications, hydrogen (or other fuel gas) generated by the cell can be stored and used for generation of electricity.

For example, after the porous polymeric membrane has been formed around current collector(s) of a microcell fiber structure, the structure can be directly passed through a solution of aqueous polymeric electrolyte, such as a solution of Nafion (5% solids in water and alcohol) polymeric electrolyte, to impregnate the pores of the porous polymeric membrane with the polymeric electrolyte. The amount of the impregnated polymeric electrolyte may be selectively varied depending on the residence time of the porous polymeric membrane in the electrolyte impregnant composition, and the number of times that the structure is repetitively exposed to the composition (i.e., in single-pass or multi-pass fashion) during processing.

On the same process line in which the electrolyte is impregnated, or alternatively in a subsequent phase of the fabrication operation, the microcell fibers in one process embodiment are dried and

impregnated with platinum as the electrocatalyst material, using a plating solution containing  $H_2[PtCl_6]$ , following which the fibers are passed through a bath of reducing agent, such as sodium borohydride ( $NaBH_4$ ), to reduce the platinum composition to elemental platinum metal.

This continuous technique according to one embodiment of the invention is used to impregnate only the outer shell of the membrane with platinum. The inner wall of the membrane is impregnated after the fibers have been potted in the vessel by pumping the platinum plating solution through the bore of the fibers.

In another embodiment, both the shell and the bore side of the fibers are impregnated after the fibers have been potted.

After the ion exchange Nafion electrolyte solution is impregnated in the pores of the membrane, the electrocatalyst is coated according to another aspect of the invention by using platinum loaded on activated carbon of suitable particle size. The platinum loading on the activated carbon particles typically is in the range of from about 5 to about 10 percent by weight. A paste is prepared consisting essentially of platinum loaded activated carbon, Nafion ionomer as the binder, and a Teflon® polytetrafluoroethylene emulsion. The paste then is coated, or alternatively extruded, on the shell side of the fibers.

Coating of the paste inside the fiber wall may be accomplished in various ways. In one approach, the paste is coextruded while the porous membrane separator element is being spun around the current collector. A second approach is to pre-extrude the paste around the current collector before inserting the current collector into the membrane fiber. As a third approach, a thin paste can be pumped into the



bore of the porous membrane separator element after the cell assembly and potting has been completed.

In another embodiment, the electrolyte is deposited inside the porous membrane separator element, and the catalyst is applied by electrodeposition from a solution containing platinum ions, by an electrolytic plating solution process, or by an electroless plating solution process.

### Corrosion Management in the Microcell Assembly

In applications of conventional fuel cell technology, current collectors generally have been limited to the use of graphite type materials. Current collectors formed of aluminum or titanium can be coated with corrosion-resistant coatings such as gold, but such coatings tend to peel and delaminate from the current collector element under the severe corrosive conditions and thermal cycles that characterize the fuel cell operation.

The use of microcell elements permits current collector materials of construction other than graphitic materials to be employed. Metal fibers utilized in microcell structures in the electrochemical cell module can be coated by variety of techniques to achieve durable corrosion resistance. Useful coating techniques for such purpose include, without limitation, electrochemical deposition, electroless coating, dipcoating, extrusion, etc., using corrosion resistant metal compositions or polymeric materials such as polyaniline.

A preferred approach for coating metal substrates for use as current collector involves use of amorphous metal compositions deposited by plasma coating techniques. In general, better corrosion resistance is attributable to the amorphous nature of the coating structure. Further, various amorphous

metal compositions generate extremely high surface areas. Examples of such high surface area metal compositions include nickel metal hydride electrocatalyst materials. The use of such high surface metal compositions coupled with the inherently high surface area of the fibrous geometry of the microcells enables such amorphous metal coatings to be effectively utilized for hydrogen storage capability in the fuel cell, a potentially significant structural and operational advantage.

As another approach to increase the corrosion resistance of metallic fiber substrates, the metal fibers can be coated with a polymeric precursor or other organic coating, and the coating then is carbonized. Carbonization of the polymer to form graphitic material on metallic fibers yields a coating that is corrosion resistant, yet possesses electrical conductivity that is higher than that of carbon or graphite alone.

The presence of pinholes in any coating application can cause corrosion and electrical disconnection of one section of the microcell from others, which in turn reduces the useful power density of the cell. In another approach, such electrical disconnection deficiencies are avoided by a fabrication method involving co-placement of a carbon fiber in the bore or on the shell side of the microcell, so that the carbon fiber is in intimate contact with the associated current collector of the microcell. With such arrangement, if the current collector is corrosively attacked in the operation of the electrochemical cell, the carbon or graphitic fiber then continues to maintain a flow of current therethrough, thereby providing electrical continuity despite even gross corrosion-mediated breakage or deterioration of the current collector element.

To enhance the service life of metallic current collector fibers in the corrosive environment of a fuel cell, the metal fiber is advantageously coated with a compound such as a polymeric material, following which the coated fiber is subjected to pyrolysis conditions for the polymeric material. The

fiber coating material is pyrolyzed and converted to carbon using techniques that are conventionally employed to form carbon fibers *per se*.

Formation of a continuous layer of carbon on a metallic current collector fiber (of any size) produces a fiber that is electrically conductive radially and longitudinally and at the same time is corrosion-resistant due to the surface layer protecting the underlying metal from corrosive attack.

Figure 46 is an elevation view of a conductor element 1002 including a metallic fiber 1004 having a polymeric compound coating 1006 on its outer surface. The fiber is coated in any suitable manner, e.g., by spraying, dip-coating, roller coating, etc.

Figure 47 shows the corresponding fiber 1002 of Figure 46 after the pyrolysis step, as comprising a pyrolyzed carbon coating 1008 on the outside surface thereof.

Concerning current collector and electrode preparation, the electrically conductive metal fibers of the microcell in one embodiment of the invention comprise copper, aluminum or titanium fibers, having a diameter in the range of from about 100 to about 10,000 microns, coated with a suitable thickness of corrosion-resistant material such as gold or platinum.

Alternatively, carbon/graphite fibers having diameter in the range of from about 100 to about 10,000 microns and having good electrical conductivity characteristics can be employed, and metallized with the electrocatalyst, e.g., platinum. Such platinum metallization is advantageously effected by contacting the fibers with a plating solution containing  $H_2[PtCl_6]$ , followed by reduction of the platinum compound to elemental platinum metal via contact with sodium borohydride ( $NaBH_4$ ).

With respect to current collectors, the presence of pinholes or coating defects causes accelerated corrosion of metallic current collectors. In consequence of such corrosion, the fiber cell can disconnect (as a result of the continuity of the conductor being impaired) and become inoperable. To avoid this disconnection of part of the microcell voltage and current, fibrous carbon current collectors advantageously are laid along the coated metallic fibers. Figure 48 shows a conductor 1010 including a fibrous carbon current collector 1014 laid along a coated metallic fiber 1012. The carbon fiber 1014 will be in intimate contact with the coated fiber 1012, as shown in Figure 48.

Figure 49 shows the fiber assembly of Figure 48 after a disconnection break of the coated metallic fiber 1012. In the event of a corrosion point break in continuity of the coated metallic fiber, the carbon fiber 1014 in contact with both sections of the corroded metal fiber 1012 provides continuity enabling the current to pass from one side to the other along the length of the carbon fiber/metallic fiber arrangement.

#### **Water Management in Microcell Assemblies**

In microcell electrochemical reactions wherein water is a reaction by-product, a feed may be humidified to prevent drying of the membrane, the microcell assembly desirably includes a water management system for addition and removal of excess water from the microcell assembly.

In general, the high surface area of microcell structures, and lower mass transfer resistance, mean that the removal of water from the microcell module is less problematic than in conventional planar fuel cell structures.

Various alternatives can be employed to further enhance the water management capacity of the microcell fuel cell module. For example, if heat exchange tubes are employed in the fuel cell assembly, comprising hollow fiber membranes coated with Nafion or other ion-exchange polymer or material that will selectively allow water permeation, and if the heat exchange liquid is water, the heat exchange tubes can be used for water supply to the fuel cell and removal of heat from the fuel cell.

One approach for water removal from the fuel cell is to provide porous plane hollow fiber membranes in the microcell bundle, in distributed fashion therein. In this structural arrangement, water will permeate through the membrane wall by a wicking action during operation of the fuel cell and will be channeled down the bore of the hollow fiber and away from the active surfaces. The resultingly channeled water then can be collected in a plenum provided in the housing containing the module, for discharge from the system.

Concerning the removal of water from fuel cells, various approaches are contemplated by the present invention. To remove water produced in the fuel cell made from fiber cells or microcells, hollow fiber membranes treated with a hydrophilic compound can be packed intermittently with fiber cells containing an electrode or current collector. Since these hollow fiber membranes are in intimate contact with the shell side of the cells and are open on the bore side, water produced in the fuel cell is absorbed by a wicking action and channeled down the bore of the membrane hollow fiber membrane away from the cells containing the electrode, thereby eliminating the water flooding in the cell.

If the module is mounted vertically, then water may be collected by gravity collection at the bottom of the cell and discharged therefrom.

Figure 50 shows a cross-section of a hollow fiber and microcell tube bundle 1020, in which the plane hollow fiber elements 1026 are interspersed with the microcell fiber elements 1022 and shell side electrodes 1024, and such hollow fiber elements are used for channeling water from the assembly.

Figure 51 is a sectional elevation view of a microcell fuel cell module 1030, including a housing 1032 containing a microcell assembly 1036 arranged vertically as shown. The housing 1032 has a flange 1034 by means of which the upper end of the housing can be removed to access the microcell assembly and other internal components of the module.

The microcell assembly 1036 is potted at its upper end by potting member 1040 leak-tightly sealed to the inner wall of the housing by O-ring sealing element 1042. In like manner, the microcell assembly 1036 is potted at its lower end by potting member 1044 leak-tightly sealed to the inner wall of the housing by O-ring sealing element 1046.

The microcell assembly 1036 engages a central feed tube 1080, which is perforate within the interior volume of the microcell assembly. Additionally, feed inlet 1060 provides feed to the bore side of the microcell elements in the assembly, from upper end volume 1048. Feed discharged at the lower end from the hollow fiber elements enters the lower end volume 1050 and is discharged from the housing from outlet 1072 or outlet 1070.

Outlet 1078 is provided for interior volume 1038 of the housing, for discharge of spent feed from the interior volume (shell side).

The lower end of housing 1032 constitutes a plenum chamber 1076 which receives access water (condensate) gravitationally flowed to such lower end of the housing, and discharged by overflow through outlet 1072 or outlet 1070.

The current collector elements at respective ends of the microcell assembly are joined to respective terminals 1082 and 1084, as illustrated.

Accordingly, the hollow fiber tubular elements employed in the microcell assembly allow permeation of excess water in to the bore passages of such hollow fibers and drainage thereof to the plenum chamber, to readily remove excess water from the electrochemical fuel cell module.

Any other suitable means or methods can be used to channel water from the microcell assembly, including elements or structures that utilize surface tension or capillarity effects to induce channelized flow of water from the microcell bundle to a collection vessel or locus. By way of example, the enhancement structure for film condensation apparatus that is described in U.S. Patent 4,253,519 issued March 3, 1981 to Leslie C. Kun and Elias G. Ragi is usefully employed as an overlay structure on the microcell fibers or bundles or sub-bundles comprising same, to effect channelized flow of liquid for recovery and discharge thereof from the fuel cell module.

In each of the foregoing approaches, the electrolyte/catalyst-impregnated coated fiber can be optionally coated with a Teflon® polytetrafluoroethylene emulsion, to impart hydrophobicity to the membrane/electrode assembly. By such expedient, water introduced or formed in the cell will be repelled from the catalyst surface, to enhance the availability of the catalyst site to the fuel or the oxidant (e.g., hydrogen, or oxygen).

While the invention has been described herein with reference to specific embodiments, features and aspects, it will be recognized that the invention is not thus limited, but rather extends in utility to other modifications, variations, applications, and embodiments, and accordingly all such other modifications, variations, applications, and embodiments are to be regarded as being within the spirit and scope of the invention.



THE CLAIMSWHAT IS CLAIMED IS:

1. A microcell assembly, wherein each microcell comprises:

an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

said assembly comprising a first cell including a first microcell sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, with each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member;

an insulating sheet for electrical isolation of the first cell from a further cell overlying the insulating sheet;

a second cell including a first microcell sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from one edge of the second sheet member, adjacent the second edge of the first sheet member, and a second sheet member of external current collectors overlying the first sheet member, with each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond the opposite edge of the first sheet member;

wherein the inner current collectors of the first cell are aligned with and electrically connected to the outer current collectors of the second cell to form a series connection therewith.

2. The microcell assembly of claim 1, wherein the collectors are interconnected by soldering, brazing, welding, conductive adhesive bonding, or melt bonding.
3. The microcell assembly of claim 1, comprising a multicell structure including plural ones of said first and second cells, arranged in an alternating manner, wherein each of adjacent cells is correspondingly serially connected.
4. The microcell assembly of claim 1, wherein the successive cells are potted at each of opposite ends to seal the shell side and bore side of the microcells.
5. A microcell module, comprising:

a gas feed chamber including a perforate plate member;

a microcell assembly as in claim 1 positioned on the perforate plate member, and potted at respective ends thereof by potting members forming respective seal faces which when the seal faces at their periphery are abuttingly reposed in a housing, form a shell and tube structural arrangement, wherein the perforate plate member is intermediately positioned between the potting members.

6. The microcell module of claim 5, circumscribingly enclosed in said shell and tube structural arrangement.

7. A microcell sub-bundle article, comprising:

a sheet assembly including a first microcell sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, with each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member;

wherein the sub-bundle has been formed by axially rolling the sheet assembly into a cylindrical pre-form, applying a porous and electrically insulative wrap to the outer cylindrical surface of the cylindrical pre-form; and potting at respective ends of the cylindrical pre-form, to yield said sub-bundle,

wherein the first and second sheet members form a cell.

8. A microcell sub-bundle article according to claim 7, further comprising a central tubular member that is perforate over an intermediate length thereof between the potted ends, and otherwise imperforate outside of the potted ends.
9. A microcell sub-bundle article according to claim 7, wherein said sheet assembly further comprises a porous, electrically insulative sheet member overlying the second sheet member, a third sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from a first edge of said third sheet member, and a fourth sheet member of external current collectors overlying the third sheet member, with each current collector of the third sheet member in contact with at least one microcell fiber of the third sheet member and extending beyond an opposite, second edge of the fourth sheet member, wherein the current collectors of the first and third sheet members are generally coextensive in length with one another at their ends, and the current collectors of the second and fourth sheet members are generally coextensive in length with one another at their ends, and wherein said ends of the second and third sheet member current collectors are electrically connected at their ends, said third and fourth sheet members forming a second cell.
10. A microcell sub-bundle article according to claim 7, comprising a plurality of microcell fiber sheets forming multiple cells.
11. A microcell sub-bundle article according to claim 7, wherein the article comprises a repeating sequence of first and second sheet members forming a multiplicity of cells, wherein each cell is separated from an adjacent cell by a porous, electrically insulative sheet member.

12. A series-connected assembly of at least two sub-bundles as in claim 7.
13. A microcell article comprising a series of microcell sub-bundle articles as in claim 11, sequentially connected in positive-to-negative electrode arrangement, having an elongate character.
14. A microcell article as in claim 13, wherein the connection comprises a living hinge member.
15. The microcell article of claim 13, wherein the connection comprises welding, brazing, soldering, conductive adhesive bonding, or melt bonding.
16. A microcell article comprising a series of microcell sub-bundle articles as in claim 11, sequentially connected in positive-to-negative electrode arrangement, in a bundle wherein component sub-bundle articles are parallelly aligned with one another in side-by-side relationship of consecutive sub-bundle articles, and the bundle has an axial dimension that substantially equal to the axial dimension of each sub-bundle article in the bundle.
17. The microcell article of claim 16, wherein the bundle is potted at respective ends.
18. A microcell article, comprising a plurality of microcell sub-bundle articles as in claim 11, arranged in side-by-side relationship, with electrodes of adjacent ones of said sub-bundle articles being electrically interconnected in positive-to-negative electrode relationship, and with the microcell article being potted at respective ends thereof.

19. A microcell article as in claim 18, wherein each sub-bundle comprises a central tubular member that is perforate over an intermediate length thereof between the potted ends, and otherwise imperforate outside of the potted ends.
20. A microcell article as in claim 19, further comprising a feed distribution manifold joined in feed relationship to the central tubular member of each of the multiple sub-bundles.
21. A microcell sub-bundle as in claim 11, wherein the potted ends define respective tubesheets, with each tubesheet having a sealable periphery.
22. A microcell module comprising a housing having mounted therein a plurality of microcell sub-bundles as in claim 21, wherein the housing comprises an interior volume bounded by respective end-plates, each end-plate having openings therein each of which is matably and sealingly engageable with a tubesheet of a corresponding sub-bundle, and wherein corresponding end-plate openings of the respective end-plates are in coaxial register with one another, said housing including a first end volume bounded by the end-plate at one end of the housing, and a second end volume bounded by the end-plate at the other end of the housing, a feed tube arranged for delivery of feed to said sub-bundles, and an outlet for discharging depleted feed from the interior volume, said housing being selectively openable to expose an end-plate at at least one of said end volumes for accessing sub-bundles mounted in said end-plate for removal thereof and installation of a replacement sub-bundle, wherein said sub-bundles in said housing are series connected with one another and connected to a terminal leak-tightly extending exteriorly of the housing.

23. A microcell module according to claim 22, further comprising a feed distribution manifold connected with said feed tube and joined in feed relationship to the central tubular member of each of the multiple sub-bundles.
24. A microcell module according to claim 22, wherein the feed tube extends through one of the end volumes and is joined in closed gas flow communication with the interior volume.
25. A microcell module according to claim 22, wherein the respective end-plates have mounted therein less than a full complement of sub-bundles, and wherein an end-plate opening not having a sub-bundle mounted therein is leak-tightly sealed with a closure plate at corresponding openings in the respective end-plates.
26. A method of making an electrochemical cell device, comprising:

forming a layer structure of sheets including a first sheet of fibrous microcell elements arranged in parallel side-by-side arrangement as a first sheet, and a second sheet comprising a parallelly aligned spaced-apart arrangement of external current collector elements in a second sheet;

mating the first and second sheets in longitudinally off-set relationship to one another, so that said external current collectors extend beyond an edge of the first sheet, and internal current collectors of said fibrous microcell elements extend beyond an opposite edge of the second sheet;

adding corresponding layers of corresponding first and second sheets to the initial layer of first and second sheets, and disposing a porous insulative sheet between each of the respective layers, to form a multilayer structure;

shaping said multilayer structure into a predetermined sub-bundle shape, and potting same to impart a permanent shape thereto, wherein said permanent shape provides localized conformations of internal and external current collectors;

fabricating a plurality of sub-bundles in corresponding manner;

connecting said sub-bundles in sequence to form a series arrangement of sub-bundles;  
and

shaping the series-connected sub-bundles to form a bundle assembly.

27. A method of fabricating a microcell assembly, comprising:

forming a first layer including a first microcell sheet member comprising a plurality of fibrous microcell elements parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said fibrous microcell elements axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, positioning each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member;



disposing an insulating sheet on said first layer;

forming a second layer including a first microcell sheet member comprising a plurality of fibrous microcell elements parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said fibrous microcell elements axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, positioning each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member; and

electrically connecting the inner current collectors of the first layer with the outer current collectors of the second layer to form a series connection therewith.

28. The method of claim 27, wherein the current collectors are interconnected by soldering, brazing, welding, conductive adhesive bonding, or melt bonding.
29. The method of claim 27, comprising forming an assembly comprising a multiplicity of said first and second layers in alternating sequence, and electrically interconnecting successive layers in series relationship to one another.
30. The method of claim 27, further comprising potting the microcell assembly to seal the shell side and bore side of the fibrous microcell elements from one another.
31. A method of fabricating a microcell module, comprising:

providing a gas feed chamber including a perforate plate member;  
positioning on the perforated plate member a microcell assembly comprising a plurality of fibrous microcell elements and associated external current collectors defining a plurality of microcells, and potting the microcell assembly at respective ends thereof by potting members forming respective seal faces which when the seal faces at their periphery are abuttingly reposed in a housing, form a shell and tube structural arrangement, wherein the perforated plate member is intermediately positioned between the potting members.

32. A method according to claim 31, comprising circumscribingly enclosing the microcell module in a housing to form said shell and tube structural arrangement.

33. A method of fabricating a microcell sub-bundle article, comprising:

forming a sheet assembly including a first microcell sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, with each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member;

axially rolling the sheet assembly into a cylindrical pre-form, applying a porous and electrically insulative wrap to the outer cylindrical surface of the cylindrical pre-form; and potting respective ends of the cylindrical pre-form, to yield said sub-bundle,

wherein the first and second sheet members form a cell.

34. A method according to claim 33, wherein the sheet assembly is rolled on a central tubular member that is perforate over an intermediate length thereof between the potted ends, and otherwise imperforate outside of the potted ends.

35. A method according to claim 34, further comprising fabricating said sheet assembly to further comprise a porous, electrically insulative sheet member overlying the second sheet member, a third sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from a first edge of said third sheet member, and a fourth sheet member of external current collectors overlying the third sheet member, with each current collector of the third sheet member in contact with at least one microcell fiber of the third sheet member and extending beyond an opposite, second edge of the fourth sheet member, wherein the current collectors of the first and third sheet members are generally coextensive in length with one another at their ends, and the current collectors of the second and fourth sheet members are generally coextensive in length with one another at their ends, and wherein said ends of the second and third sheet member current collectors are electrically connected at their ends, said third and fourth sheet members forming a second cell.

36. A method according to claim 34, comprising fabricating the microcell sub-bundle article with a plurality of microcell fiber sheets forming multiple cells.

37. A method according to claim 34, comprising fabricating a repeating sequence of first and second sheet members forming a multiplicity of cells, and disposing a porous, electrically insulative sheet between successive cells.

38. A method according to claim 34, comprising electrically connecting at least two sub-bundles in series.

39. A method according to claim 38, wherein said at least two sub-bundles are sequentially connected in positive-to-negative electrode arrangement, having an elongate character.

40. A method according to claim 38, wherein said step of electrically connecting at least two sub-bundles in series, comprises interconnecting successive sub-bundles with a connector comprising a living hinge member.

41. A method according to claim 38, wherein said step of electrically connecting at least two sub-bundles in series, comprises welding, brazing, soldering, conductive adhesive bonding, or melt bonding.

42. A method of fabricating a microcell article comprising a series of microcell sub-bundle articles, said method including fabricating a plurality of microcell sub-bundle articles having positive electrode and negative electrode structures, parallelly aligning said sub-bundle articles with one another in side-by-side relationship of consecutive sub-bundle articles, thereby forming a bundle of said sub-bundle articles, and electrically interconnecting the sub-bundle articles in series.

43. The method of claim 42, further comprising potting the bundle at respective ends.
44. The microcell assembly of claim 1, wherein the membrane separator is fabricated from a material selected from the group consisting of semi-permeable, ion-exchange membranes, and a porous membrane coated on a shell or bore side thereof with a perm-selective or an ion-exchange polymer.
45. The method of claim 27, wherein each of said fibrous microcell elements comprises a porous membrane separator, wherein the membrane separator is fabricated from a material selected from the group consisting of semi-permeable, ion-exchange membranes, and a porous membrane coated on a shell or bore side thereof with a perm-selective or an ion-exchange polymer.
46. A fibrous microcell structure comprising at least one electrically conductive fibrous element circumscribed by a porous membrane separator having coated, impregnated or extruded at an inner surface thereof a first electrocatalyst layer having an electrically conductive hydrogen- or oxygen-permselective membrane thereon, with an electrolyte disposed in porosity of the porous membrane separator, said structure including a central lumen therethrough including said at least one electrically conductive fibrous element and interstitial volume accommodating flow of feed through the lumen, and said porous membrane separator at an outer surface being in contact with an electrocatalyst and at least one electrically conductive fiber.
47. The fibrous microcell structure according to claim 46 wherein the outer surface of the porous membrane separator has coated, impregnated or has extruded thereon a second electrocatalyst layer.

48. The fibrous microcell structure according to claim 46, wherein the electrocatalyst layer comprises an electrocatalyst in combination with at least one of an electrically conductive material and a hydrophobicity-imparting material.
49. The fibrous microcell structure according to claim 46, having an outer diameter in the range of from about 100 microns to about 10 millimeters.
50. The fibrous microcell structure according to claim 46, wherein the permselective membrane is applied to the porous membrane separator by a method selected from the group consisting of electroless plating, electrochemical deposition, extrusion, vapor deposition, solution deposition.
51. The fibrous microcell structure according to claim 46, wherein the permselective membrane comprises a material selected from the group consisting of metals and electrically conductive polymeric materials.
52. The fibrous microcell structure according to claim 46, wherein the permselective membrane comprises palladium.
53. The fibrous microcell structure according to claim 46, wherein the hydrophobicity-imparting material comprises a fluoropolymer.
54. The fibrous microcell structure according to claim 53, wherein the hydrophobicity-imparting material comprises polytetrafluoroethylene.

55. A fibrous microcell structure comprising an inner porous membrane separator bounding a central lumen and having coated, impregnated or extruded at an inner surface thereof a hydrogen- or oxygen-permselective membrane thereon, with a first electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface thereof, to thereby form an interior structure, and an outer porous membrane separator encapsulating the interior structure, and with a second electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface of the outer porous membrane separator, with an electrolyte disposed in porosity of the outer porous membrane separator.

56. The fibrous microcell structure according to claim 55 wherein the hydrogen- or oxygen-permselective membrane is formed of a material selected from the group consisting of cellulose esters, polyimides, polysulfones, and palladium.

57. A fibrous microcell structure according to claim 55 wherein the first electrocatalyst material is coated, impregnated or extruded at the outer surface of the inner porous membrane separator.

58. The fibrous microcell structure according to claim 55 wherein the second electrocatalyst material is coated, impregnated or extruded at the outer surface of the outer porous membrane separator.

59. The fibrous microcell structure according to claim 55, wherein at least one of the first and second electrocatalyst layers comprises an electrocatalyst in combination with at least one of an electrically conductive material and a hydrophobicity-imparting material.

60. The fibrous microcell structure according to claim 55, having an outer diameter in the range of from about 100 microns to about 10 millimeters.
61. The fibrous microcell structure according to claim 55, wherein the permselective membrane is applied to the inner porous membrane separator by a method selected from the group consisting of electroless plating, electrochemical deposition, extrusion, vapor deposition, and solution deposition.
62. The fibrous microcell structure according to claim 55, wherein the permselective membrane comprises a material selected from the group consisting of metals and electrically conductive polymeric materials.
63. The fibrous microcell structure according to claim 55, wherein the permselective membrane comprises palladium.
64. A fibrous microcell structure according to claim 59, wherein the hydrophobicity-imparting material comprises a fluoropolymer.
65. The fibrous microcell structure according to claim 64, wherein the hydrophobicity-imparting material comprises polytetrafluoroethylene.
66. The fibrous microcell structure according to claim 58, having an electrically conductive hydrogen- or oxygen-permselective membrane on the second electrocatalyst material.
67. The fibrous microcell structure according to claim 66 wherein the inner membrane separator is electrically conductive.



68. A fibrous microcell structure according to claim 67, devoid of current collector fibers.

69. A fibrous microcell structure comprising an inner porous membrane separator bounding a central lumen and having coated, impregnated or extruded at an inner surface thereof a reformer catalyst thereon, with a hydrogen- or oxygen-permselective membrane at an outer surface thereof, and a first electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface thereof, to thereby form an interior structure, and an outer porous membrane separator encapsulating the interior structure, and with a second electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface of the outer porous membrane separator, with an electrolyte disposed in porosity of the outer porous membrane separator.

70. The fibrous microcell structure according to claim 69, wherein the reformer catalyst comprises a metal oxide.

71. The fibrous microcell structure according to claim 69, wherein the reformer catalyst comprises a metal oxide selected from the group consisting of copper oxide, zinc oxide and mixtures thereof.

72. The fibrous microcell structure according to claim 69, wherein the reformer catalyst is catalytically effective to convert CO to CO<sub>2</sub>.

73. The fibrous microcell structure according to claim 69, wherein the porous membrane separator is formed of a material selected from the group consisting of glasses, ceramics and polymeric materials.

74. An electrochemical apparatus comprising at least one fibrous microcell structure as in claim 46.

75. An electrochemical apparatus comprising at least one fibrous microcell structure as in claim 55.

76. An electrochemical apparatus comprising at least one fibrous microcell structure as in claim 56.

77. An electrochemical apparatus comprising at least one fibrous microcell structure as in claim 57.

78. A method of making a fibrous microcell structure including the steps of: circumscribing at least one electrically conductive fibrous element with a porous membrane separator; coating, impregnating or extruding at an inner surface of the porous membrane separator a first electrocatalyst layer; forming an electrically conductive hydrogen- or oxygen-permselective membrane on the first electrocatalyst layer; disposing an electrolyte in porosity of the porous membrane separator; with said steps being carried out so that said structure includes a central lumen therethrough including said at least one electrically conductive fibrous element and interstitial volume accommodating flow of feed through the lumen, and disposing an outer surface of said porous membrane separator in contact with an electrocatalyst and at least one electrically conductive fiber.

79. The method of claim 78 comprising coating, impregnating or has extruding on the outer surface of the porous membrane separator a second electrocatalyst layer.

80. The method of claim 78, wherein the electrocatalyst layer comprises an electrocatalyst in combination with at least one of an electrically conductive material and a hydrophobicity-imparting material.

81. The method of claim 78, wherein the fibrous microcell structure has an outer diameter in the range of from about 100 microns to about 10 millimeters.

82. The method of claim 78, wherein the permselective membrane is applied to the porous membrane separator by a method selected from the group consisting of electroless plating, electrochemical deposition, extrusion, vapor deposition, solution deposition.

83. The method of claim 78, wherein the permselective membrane comprises a material selected from the group consisting of metals and electrically conductive polymeric materials.

84. The method of claim 87, wherein the permselective membrane comprises palladium.

85. The method of claim 80, wherein the hydrophobicity-imparting material comprises a fluoropolymer.

86. The method of claim 80, wherein the hydrophobicity-imparting material comprises polytetrafluoroethylene.

87. A method of making a fibrous microcell structure comprising providing an inner porous membrane separator bounding a central lumen and coating, impregnating or extruding at an inner surface thereof a hydrogen- or oxygen-permselective membrane thereon, and disposing a first

electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface thereof, to thereby form an interior structure, encapsulating the interior structure with an outer porous membrane separator, placing a second electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface of the outer porous membrane separator, and disposing an electrolyte in porosity of the outer porous membrane separator.

88. The method of claim 87, wherein the hydrogen- or oxygen-permselective membrane is formed of a material selected from the group consisting of cellulose esters, polyimides, polysulfones, and palladium.

89. The method of claim 87, wherein the first electrocatalyst material is coated, impregnated or extruded at the outer surface of the inner porous membrane separator.

90. The method of claim 87, wherein the second electrocatalyst material is coated, impregnated or extruded at the outer surface of the outer porous membrane separator.

91. The method of claim 87, wherein at least one of the first and second electrocatalyst layers comprises an electrocatalyst in combination with at least one of an electrically conductive material and a hydrophobicity-imparting material.

92. The method of claim 87, wherein the fibrous microcell structure has an outer diameter in the range of from about 100 microns to about 10 millimeters.

93. The method of claim 87, wherein the permselective membrane is applied to the inner porous membrane separator by a method selected from the group consisting of electroless plating, electrochemical deposition, extrusion, vapor deposition, solution deposition.
94. The method of claim 87, wherein the permselective membrane comprises a material selected from the group consisting of metals and electrically conductive polymeric materials.
95. The method of claim 87, wherein the permselective membrane comprises palladium.
96. The method according to claim 91, wherein the hydrophobicity-imparting material comprises a fluoropolymer.
97. The method according to claim 91, wherein the hydrophobicity-imparting material comprises polytetrafluoroethylene.
98. The method according to claim 90, having an electrically conductive hydrogen- or oxygen-permselective membrane on the second electrocatalyst material.
99. The method according to claim 98 wherein the inner membrane separator is electrically conductive.
100. The method according to claim 99, devoid of current collector fibers.
101. A method of making a fibrous microcell structure comprising: providing an inner porous membrane separator bounding a central lumen; coating, impregnating or extruding at an inner surface

thereof a reformer catalyst thereon, forming a hydrogen- or oxygen-permselective membrane at an outer surface thereof, and placing a first electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface thereof, to thereby form an interior structure, encapsulating the interior structure with an outer porous membrane separator, disposing a second electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface of the outer porous membrane separator, and disposing an electrolyte in porosity of the outer porous membrane separator.

102. The method according to claim 101, wherein the reformer catalyst comprises a metal oxide.

103. The method according to claim 101, wherein the reformer catalyst comprises a metal oxide selected from the group consisting of copper oxide, zinc oxide and mixtures thereof.

104. The method according to claim 101, wherein the reformer catalyst is catalytically effective to convert CO to CO<sub>2</sub>.

105. The method according to claim 101, wherein the porous membrane separator is formed of a material selected from the group consisting of glasses, ceramics and polymeric materials.

106. A process system comprising:

a supply of microcell precursor comprising at least one current collector within a porous membrane separator arranged in dispensing relationship;

a liquid contacting unit arranged for receiving microcell precursor from said supply, wherein dispensed microcell precursor is contacted with at least one of electrolyte, electrocatalyst, electrocatalyst reducing agent, and hydrophicity-imparting material;

optionally a dryer unit arranged for receiving microcell precursor from the liquid contacting unit for drying the microcell precursor; and

collection means for collecting the precursor after liquid contacting and optional drying thereof.

107. A process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an ion exchange polymer solution.

108. A process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst solution.

109. A process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst reducing solution.

110. A process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst solution comprising platonic acid solution.

111. The process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst reducing agent comprising sodium borohydride.

112. The process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with a hydrophobicity-imparting material comprising a PTFE emulsion.

113. The process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an ink solution comprising an electrocatalyst, carbon powder, ion exchange polymer, and a hydrophobicity-imparting material.

114. A process for manufacturing a fiber microcell article, comprising the steps of:

- disposing electrolyte material in pores of a microcell precursor article;
- drying the precursor article;
- applying electrocatalyst material in the form of solution or ink slurry to the precursor;
- drying the precursor article;
- reducing the electrocatalyst material to a catalytically active form.

115. The process according to claim 114, wherein the electrocatalyst material comprises an ink slurry and said slurry is applied to the precursor article by extrusion.

116. The process according to claim 114, wherein the microcell precursor article is formed by passage of a strand or tow of a fibrous current collector through the bore-forming tube of a hollow fiber extrusion mold with gaseous or liquid coagulants.

117. The process according to claim 114, wherein the microcell precursor article is formed by the steps of:

- providing a fiber or tow of current collector(s);



applying to said fiber or tow a porous membrane-forming material;  
processing the fiber or tow having the porous membrane-forming material thereon, to  
form porosity therein.

118. The process according to claim 117, wherein the porous membrane-forming material has porosity in a range suitable for application selected from the group consisting of ultrafiltration, microfiltration and reverse osmosis.

119. The process according to claim 117, wherein the porous membrane-forming material is formed from a material selected from the group consisting of polymeric materials, glasses, ceramics, and combinations thereof.

120. The process according to claim 117, wherein the porous membrane-forming material is applied by a method selected from the group consisting of wet spinning and melt spinning.

121. The process according to claim 117, wherein the porous membrane-forming material comprises a dope including a backbone component and a leachable component that upon removal by leaching yields voids constituting porosity of the porous membrane.

122. The process according to claim 117, wherein the porous membrane-forming material comprises a dope, and wherein a coagulating agent is applied to the dope on at least one of an inner surface and outer surface of the applied dope.

123. The process according to claim 117, wherein the porous membrane-forming material is applied by melt-spinning and wherein the fiber or tow having the melt-spinning material applied thereto is contacted with a quench medium.

124. The process according to claim 122, wherein an electrocatalyst ink paste is coextruded with the coagulating agent on said inner surface.

125. The process according to claim 117, further comprising the steps of:

coating the porous membrane separator with one of a perm-selective membrane material and an ion-exchange polymer.

126. The process according to claim 117, further comprising fabricating a microcell module comprising a plurality of the precursor articles wherein the precursor articles are potted and sealed to form a shell-and-tube conformation with precursor articles aligned with one another, and flowing through at least one of the shell side and the tube side of said shell-and-tube conformation an electrocatalyst solution, electrocatalyst ink or a reducing agent.

127. The process according to claim 117, further comprising fabricating a microcell module comprising a plurality of the precursor articles wherein the precursor articles are potted and sealed to form a shell-and-tube conformation with precursor articles aligned with one another, and electrocatalyst material is applied to at one of the shell side and the tube side of said shell-and-tube conformation in situ.

128. The process according to claim 127 wherein the electrocatalyst material is applied to the shell-and-tube conformation by a method selected from the group consisting of electroless plating, electrochemical deposition, extrusion, vapor deposition, solution deposition.

129. The process of claim 117 wherein the membrane separator comprises a membrane selected from the group consisting of semi-permeable membranes and ion exchange membranes.

130. An electrochemical cell module, comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

with the microcell assembly including a plurality of hollow tubular heat exchange elements arranged for flow of a coolant medium through a central lumen thereof, with the hollow tubular heat exchange elements being distributed in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module;

a source of said coolant medium; and

flow circuitry interconnecting the source of said coolant medium and said hollow tubular heat exchange elements.

131. The electrochemical cell module of claim 130, wherein said coolant medium is a liquid coolant.

132. The electrochemical cell module of claim 130, wherein said coolant medium is a gas.

133. The electrochemical cell module of claim 130, wherein said flow circuitry comprises a manifold at each of opposite ends of said assembly of microcells, and said hollow tubular heat exchange elements are coupled in flow communication at opposite ends thereof with a corresponding manifold, and a pump joined to said flow circuitry for effecting flow of said coolant medium through the hollow tubular heat exchange elements in the module, to remove heat generated by said assembly by electrochemical reaction in the microcells.

134. The electrochemical cell module of claim 130, wherein the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a first potting member through which open ends of the microcell fibers are exposed for fluid flow therethrough, with the first potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first potting member, and said tubular heat exchange elements further potted in a second potting member in spaced relationship to the first potting member, to define between the first and second potting members a closed volume of the housing, and with a housing inlet communicating with the closed volume, for introduction of feed into the closed volume, for flow through the assembly on the bore side of the microcell fibers thereof, and wherein said second potting

member defines with the housing a closed end volume, with said tubular heat exchange elements extending through the second potting member and terminating in the closed end volume at open ends of the heat exchange elements, and with a coolant medium inlet communicating with the closed end volume, for introduction of coolant medium into the closed end volume, for flow of coolant axially through the tubular heat exchange elements in the assembly;

with a second end of the assembly potted in a first opposite potting member through which open opposite ends of the microcell fibers are exposed for fluid flow therethrough, with the first opposite potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first opposite potting member, and said tubular heat exchange elements further potted in a second opposite potting member in spaced relationship to the first opposite potting member, to define between the first and second opposite potting members a closed opposite volume of the housing, and with a housing outlet communicating with the closed volume, for discharge of depleted fuel from the closed volume, and wherein said second opposite potting member defines with the housing a closed opposite end volume, with said tubular heat exchange elements extending through the second opposite potting member and terminating in the closed opposite end volume at open ends of the heat exchange elements, and with a coolant medium outlet communicating with the closed opposite end volume, for discharge of coolant medium from the closed opposite end volume, for removal of heat of electrochemical reaction from the assembly;

wherein said current collectors at their ends are joined in series or parallel with one another to form a terminal leak-tightly extending out of the housing;

and a feed tube leak-tightly joined in feed communication with the shell side of the microcells in said assembly.

135. The electrochemical cell module of claim 133, wherein the feed tube extends axially into the housing, and through the first and second potting members.

136. The electrochemical cell module of claim 133, wherein the current collectors extending axially of the first potting member are either bore-side current collectors or shell-side current collectors, and the current collectors extending axially of the first opposite potting member are either shell-side current collectors or bore-side current collectors, opposite to that of the current collectors extending axially of the first potting member.

137. The electrochemical cell module of claim 133, wherein each of said current collectors at an opposite end thereof either (a) terminates in a corresponding closed volume between a first and second potting member, and is distinct from said tubular heat exchange elements or (b) terminates in an end volume, and is a said tubular heat exchange element, and

wherein each of said current collectors at an opposite end thereof is connected in series or parallel with ends of other current collectors to form a terminal leak-tightly extending out of the housing.

138. The electrochemical cell module of claim 133, further comprising (i) an oxidant inlet communicating with the assembly in the housing for flow of oxidant on one of the shell side and bore side of the microcell fibers in the assembly, opposite to the side receiving feed, and (ii) a spent oxidant outlet communicating with the assembly in the housing for flow of spent oxidant out of the housing.

139. The electrochemical cell module of claim 133, wherein the housing comprises separable assembly accommodating removal of a separable part thereof to access an interior volume and components of the module.

140. The electrochemical cell module of claim 133, wherein the heat exchange elements have a cross-sectional diameter of from about 100 microns to about 10 centimeters.

141. The electrochemical cell module of claim 133, wherein the heat exchange elements and the current collectors are separate and distinct elements.

142. An electrochemical cell module, comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator, and

an outer electrode,

wherein the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a first potting member through which open ends of the microcell fibers are

exposed for fluid flow therethrough, with the first potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors constituting heat exchange elements and extending axially of the first potting member and further potted in a second potting member in spaced relationship to the first potting member, to define between the first and second potting members a closed volume of the housing, and with a housing inlet communicating with the closed volume, for introduction of feed into the closed volume, for flow through the assembly on the bore side of the microcell fibers thereof, and wherein said second potting member defines with the housing a closed end volume, with the current collectors constituting heat exchange elements extending through the second potting member and terminating in the closed end volume at open ends thereof, and with a coolant medium inlet communicating with the closed end volume, for introduction of coolant medium into the closed end volume for flow through the current collectors constituting heat exchange elements, to remove heat of electrochemical reaction from the assembly;

with a second end of the assembly potted in an opposite potting member through which open opposite ends of the microcell fibers are exposed for fluid flow therethrough, with the opposite potting member isolating the shell side of the microcell fibers from the bore side thereof, and with opposite current collectors extending axially of the opposite potting member and current collections constituting heat exchange elements terminating at the opposite potting number, and with a housing outlet communicating with the closed volume, for discharge of depleted fuel and coolant medium from the closed volume, for removal of heat of electrochemical reaction from the assembly;

and wherein said current collectors at their ends are joined in series or parallel with one another to form a terminal leak-tightly extending out of the housing.



143. An electrochemical cell module, comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

wherein the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a potting member through which open ends of the microcell fibers are exposed for fluid flow therethrough, with the potting member isolating the shell side of the microcell fibers from the bore side thereof to form a closed end volume, and with current collectors constituting heat exchange elements and extending axially of the potting member into the closed end volume, and coupled to at least one heat exchange passage in the housing, with said at least one heat exchange passage being arranged for flow of a coolant medium therethrough, and with a housing inlet communicating with the closed end volume, for introduction of feed into the closed end volume, for flow through the assembly on the bore side of the microcell fibers thereof;

with a second end of the assembly potted in an opposite potting member through which open opposite ends of the microcell fibers are exposed for fluid flow therethrough, with the opposite potting member isolating the shell side of the microcell fibers from the bore side thereof to form a closed end volume isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors constituting heat exchange elements and extending axially of the opposite potting member into the closed end volume, and coupled to at least one second heat exchange passage in the housing, with said at least one second heat exchange passage being arranged for flow of a coolant medium therethrough, and with a housing outlet communicating with the closed end volume, for discharge of depleted fuel from the closed end volume;

and wherein said current collectors at their ends are joined in series or parallel with one another to form a terminal leak-tightly extending out of the housing.

144. The electrochemical cell module of claim 142, wherein the first and second heat exchange passages are interconnected with one another.

145. The electrochemical cell module of claim 142, wherein the assembly comprises a multiplicity of component microcell sub-bundles and said sub-bundles are joined in series arrangement with one another in said array.

146. The electrochemical cell module of claim 130, wherein the tubular heat exchange elements are distributed between microcell sub-bundles as intra-sub-bundle heat exchange elements.

147. An electrochemical cell module, comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode active material,

a microporous membrane separator in contact with the inner electrode active element,

an electrolyte in pores of the microporous membrane separator,

an outer electrode active element,

with each of the inner and outer electrode active elements comprising at least one of electrode, current collector and electrocatalyst components, and said assembly including electrode or current collector components extending externally of the assembly to end portions thereof;

wherein the assembly is contained in a housing including a coolant reservoir;

a coolant in the coolant reservoir; and

said end portions of said electrode or current collector components being coupled in solid heat conduction relationship with said coolant, to enable solid conduction transfer of heat from said assembly of microcells through said electrode or current collector components to the coolant, to thereby remove heat generated by electrochemical reaction in said microcells during operation of the module.

148. The electrochemical cell module of claim 142, wherein said heat exchange elements are formed of a material of construction selected from the group consisting of metals, metals coated with corrosion resistant material, graphite and polymeric materials.

149. The electrochemical cell module of claim 142, wherein said microcells have a size of from about 100 microns to about 10 mm.

150. The electrochemical cell module of claim 142, wherein said microcells have a size of from about 100 microns to about 10 mm.

151. The electrochemical cell module of claim 142, wherein the coolant medium is a gas or liquid.

152. The electrochemical cell module of claim 142, wherein said potting members are formed of a material of construction selected from the group consisting of epoxy, polyurethane, bismaleimide, rubber, and elastomer materials.

153. A microcell module comprising an assembly of microcells wherein each microcell includes:

an inner electrode active material,

a microporous membrane separator in contact with the inner electrode active element,

an electrolyte in pores of the microporous membrane separator, and

an outer electrode active element,

with each of the inner and outer electrode active elements comprising at least one of electrode, current collector and electrocatalyst components, and said microcell including an elongate electrode or current collector;

means for extracting heat from the assembly selected from the group consisting of:

- (a) hollow tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements do not constitute current collectors;
- (b) hollow tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements constitute current collectors; and
- (c) solid current collectors extending from the assembly of microcells and coupled in heat exchange relationship with a coolant medium.

154. A process for generating electrochemical energy, comprising:

(A) providing an electrochemical cell module, comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

with the microcell assembly including a plurality of hollow tubular heat exchange elements arranged for flow of a coolant medium through a central lumen thereof, with the hollow tubular heat exchange elements being distributed in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module;

a source of said coolant medium;

flow circuitry interconnecting the source of said coolant medium and said hollow tubular heat exchange elements;

- (B) providing fuel to the electrochemical cell module to one of the shell side and bore side of the microcells in said assembly;
- (C) concurrently providing oxidant to the electrochemical cell module to the opposite one of the shell side and bore side of the microcells in said assembly, relative to the side receiving fuel, and thereby effecting electrochemical reaction to generate electrical energy and heat;
- (D) discharging depleted feed from the electrochemical cell module;
- (E) flowing said coolant medium from said source of same through said flow circuitry and said hollow tubular heat exchange elements to remove heat from the electrochemical cell module;
- (F) discharging said coolant medium from the module.

155. A process according to claim 154, further comprising the steps of:

- (G) flowing the discharged coolant medium through a heat exchanger to remove sensible heat therefrom and yield coolant medium of lower temperature; and
- (H) recirculating the lower temperature coolant medium to the module for flow through the hollow tubular heat exchange elements.

156. A process according to claim 154, wherein the coolant medium comprises water.

157. A process according to claim 154, wherein the coolant medium comprises an aqueous glycol solution.

158. A process according to claim 154, wherein at least one of the shell and tube sides is at superatmospheric pressure.

159. A method of thermally managing operation of an electrochemical cell module comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

said method comprising disposing in the microcell assembly a plurality of hollow fiber heat exchange elements arranged for flow of a coolant medium through a central lumen thereof, with the hollow fiber heat exchange elements being distributed in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module; and

flowing a coolant medium through said hollow fiber heat exchange elements during electrochemical reaction in the microcell assembly.

160. The method of claim 159, wherein said coolant medium is a liquid coolant.

161. The method of claim 159, wherein said coolant medium is a gas.

162. The method of claim 159, wherein:

the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a first potting member through which open ends of the microcell fibers are exposed for fluid flow therethrough, with the first potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first potting member, a second potting member in spaced relationship to the first potting member, to define between the first and second potting members a closed volume of the housing, and with a housing inlet communicating with the closed volume, for introduction of feed into the closed volume, for flow through the assembly on the bore side of the microcell elements thereof, and wherein said second potting member defines with the housing a closed end volume, with said heat exchange elements extending through the second potting member and terminating in the closed end volume at open ends of the heat exchange elements, and with a coolant medium inlet communicating with the closed end volume, for introduction of



coolant medium into the closed end volume, for flow of coolant axially through the heat exchange elements in the assembly;

a second end of the assembly is potted in a first opposite potting member through which open opposite ends of the microcell elements are exposed for fluid flow therethrough, with the first opposite potting member isolating the shell side of the microcell elements from the bore side thereof, and with current collectors extending axially of the first opposite potting member, a second opposite potting member in spaced relationship to the first opposite potting member, to define between the first and second opposite potting members a closed opposite volume of the housing, and with a housing outlet communicating with the closed volume, for discharge of depleted fuel from the closed volume, and wherein said second opposite potting member defines with the housing a closed opposite end volume, with said heat exchange elements extending through the second opposite potting member and terminating in the closed opposite end volume at open ends of the heat exchange elements, and with a coolant medium outlet communicating with the closed opposite end volume, for discharge of coolant medium from the closed opposite end volume, for removal of heat of electrochemical reaction from the assembly;

said current collectors at their ends are joined in series or parallel with one another to form a terminal leak-tightly extending out of the housing;

and a feed tube is leak-tightly joined in feed communication with the shell side of the microcells in said assembly.

163. The method of claim 162, wherein the feed tube extends axially into the housing, and through the first and second potting members.

164. The method of claim 162, wherein the current collectors extending axially of the first potting member are either bore-side current collectors or shell-side current collectors, and the current collectors extending axially of the first opposite potting member are either shell-side current collectors or bore-side current collectors, opposite to that of the current collectors extending axially of the first potting member.

165. The method of claim 162, wherein each of said current collectors at an outer end thereof terminates in a corresponding closed volume between a first and second potting member, and at said end is connected in series or parallel with ends of other current collectors to form a terminal leak-tightly extending out of the housing.

166. The method of claim 162, further comprising (i) an oxidant inlet communicating with the assembly in the housing for flow of oxidant on one of the shell side and bore side of the microcell elements in the assembly, opposite to the side receiving feed, and (ii) a spent oxidant outlet communicating with the assembly in the housing for flow of spent oxidant out of the housing.

167. The method of claim 162, further comprising fabricating the housing as a separable assembly accommodating removal of a separable part thereof to access an interior volume and components of the module.

168. The method of claim 162, wherein the heat exchange elements comprise current collectors for the assembly.

169. The method of claim 162, wherein the heat exchange elements have a cross-sectional diameter of from about 100 microns to about 10 centimeters.

170. The method of claim 162, wherein the heat exchange elements and the current collectors are separate and distinct elements.

171. A method of generating electrochemical energy, including the steps of:

fabricating an electrochemical cell module comprising a plurality of fibrous microcell elements in an assembly including internal and external current collectors extending outwardly therefrom;

operating said electrochemical cell module to generate electrochemical energy; and

extracting heat from at least one of said internal and external current collectors during said operating, to thereby remove heat of electrochemical reaction from said electrochemical cell module.

172. The method of claim 171, wherein current collectors are coupled to at least one heat exchange passage and further comprising flowing a coolant medium through said heat exchange passage.

173. The method of claim 171, wherein said assembly comprises a series arrangement of microcells.

174. A method of generating electrochemical energy in an electrochemical cell module, wherein said electrochemical cell module comprises: a multiplicity of microcells in an assembly, each microcell comprising an inner electrode active material, a microporous membrane separator in contact with the inner electrode active element, an electrolyte in pores of the microporous membrane separator, and an outer electrode active element, with each of the inner and outer electrode active elements comprising at least one of electrode, current collector and electrocatalyst components, and said assembly includes electrode or current collector components extending externally of the assembly to end portions thereof;

said method comprising:

mounting the assembly in a housing including a coolant reservoir with the end portions of said electrode or current collector components positioned in the reservoir; and

providing a coolant in the coolant reservoir to immerse the end portions of the electrode or current collector elements in the coolant, to enable solid conduction transfer of heat from said assembly of microcells through said electrode or current collector components to the coolant, to thereby remove heat generated by electrochemical reaction in said microcells during operation of the module.

175. A method of thermal management of a microcell module comprising an assembly of microcells wherein each microcell includes:

an inner electrode active material,

a microporous membrane separator in contact with the inner electrode active element,

an electrolyte in pores of the microporous membrane separator, and

an outer electrode active element,

with each of the inner and outer electrode active elements comprising at least one of electrode, current collector and electrocatalyst components, and said microcell including an elongate electrode or current collector;

said method comprising extracting heat from the assembly by use of a means selected from the group consisting of:

- (d) hollow tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements do not constitute current collectors;
- (e) hollow tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements constitute current collectors; and

solid current collectors extending from the assembly of microcells and coupled in heat exchange relationship with a coolant medium.

176. An electrochemical device comprising water-permeable membrane hollow fibers distributed in an assembly including a plurality of microcells potted at respective ends of the assembly and disposed within a housing wherein the potted respective ends bound an interior volume therebetween, and wherein the hollow fibers are parallelly aligned with microcells of the assembly, with each hollow fiber having a first open end extending through the tubesheet exteriorly of the interior volume and the other end terminating at or before the opposite potting member, whereby the hollow fibers are arranged to absorb water produced in the electrochemical reaction by wicking action and channeling water away

from the locus of electrochemical reaction by permeation through the wall of the hollow fiber and flow thereof through the bore of the hollow fiber to a collection locus in the housing outside of the interior volume.

177. An electrochemical device according to claim 176, wherein the housing is oriented so that the microcell elements and the hollow fibers are vertically aligned, whereby the collection locus in the housing is at the lower end of the housing, and water in the bore of the hollow fiber flows gravitationally downwardly to the collection locus.

178. An electrochemical device according to claim 176, wherein each hollow fiber is coated on its exterior surface with a hydrophilicity-imparting agent.

179. An electrochemical device according to claim 176, wherein each hollow fiber is formed of a material selected from the group consisting of polymeric materials, glasses and ceramics.

180. An electrochemical device according to claim 176, wherein the hollow fiber has a porosity in a range suitable for application selected from the group consisting of ultrafiltration, microfiltration and reverse osmosis.

181. An electrochemical device according to claim 176, wherein the hollow fiber has an outer diameter in the range of from about 100 micrometers to about 10 millimeters.

182. An electrochemical device according to claim 176, wherein each hollow fiber is formed of a hydrophilic material.

183. An electrochemical cell module, comprising:

a multiplicity of microcells in an assembly comprising a multiplicity of component microcell sub-bundles,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

with the microcell assembly including a plurality of hollow fiber heat exchange elements arranged for flow of an aqueous coolant medium through a central lumen thereof, with the hollow fiber heat exchange elements being distributed in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module;

a source of said aqueous coolant medium;

flow circuitry interconnecting the source of said aqueous coolant medium and said hollow fiber heat exchange elements;

wherein said hollow fiber heat exchange elements comprise a water-permeable porous membrane separator, whereby water deriving from the aqueous coolant medium permeates

from the bore through the membrane separator wall into the feed stream, thereby humidifying the electrochemical reaction environment.

184. The electrochemical cell module of claim 183, wherein the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a first potting member through which open ends of the microcell fibers are exposed for fluid flow therethrough, with the first potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first potting member and said heat exchange elements further potted in a second potting member in spaced relationship to the first potting member, to define between the first and second potting members a closed volume of the housing, and with a housing inlet communicating with the closed volume, for introduction of feed into the closed volume, for flow through the assembly on the bore side of the microcell fibers thereof, and wherein said second potting member defines with the housing a closed end volume, with said heat exchange elements extending through the second potting member and terminating in the closed end volume at open ends of the heat exchange elements, and with a coolant medium inlet communicating with the closed end volume, for introduction of aqueous coolant medium into the closed end volume, for flow of coolant axially through the heat exchange elements in the assembly;

with a second end of the assembly potted in a first opposite potting member through which open opposite ends of the microcell fibers are exposed for fluid flow therethrough, with the first opposite potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first opposite potting member, and said heat exchange elements further potted in a second opposite potting member in spaced relationship to the first opposite potting member, to define between the first and second opposite potting members a closed opposite volume of the housing, and with a housing outlet



communicating with the closed volume, for discharge of depleted fuel from the closed volume, and wherein said second opposite potting member defines with the housing a closed opposite end volume, with said heat exchange elements extending through the second opposite potting member and terminating in the closed opposite end volume at open ends of the heat exchange elements, and with a coolant medium outlet communicating with the closed opposite end volume, for discharge of coolant medium from the closed opposite end volume, for removal of heat of electrochemical reaction from the assembly;

wherein said current collectors at their ends are joined in series or parallel with one another to form a terminal leak-tightly extending out of the housing;

and a feed tube leak-tightly joined in feed communication with the shell side of the microcells in said assembly.

185. The electrochemical cell module of claim 183 wherein each of the hollow fiber heat exchange elements is formed of a material comprising a water perm-selective agent.

186. The electrochemical cell module of claim 183, wherein the water perm-selective agent comprises an ion-exchange fluoropolymer.

187. An electrochemical device according to claim 183, wherein the hollow fiber has a porosity in a range suitable for application selected from the group consisting of ultrafiltration, microfiltration and reverse osmosis.

188. An electrochemical device according to claim 183, wherein the hollow fiber has an outer diameter in the range of from about 100 micrometers to about 10 millimeters.

189. A method of water management in an electrochemical device including a plurality of microcells potted at respective ends and disposed within a housing wherein the potted respective ends bound an interior volume therebetween, said method comprising arranging hollow fibers to absorb water produced in the electrochemical reaction by wicking action, channeling water away from the locus of electrochemical reaction by permeation through the wall of the hollow fiber and flowing same through the bore of the hollow fiber to a collection locus in the housing outside of the interior volume.

190. A method according to claim 189, wherein the microcell elements and the hollow fibers are vertically aligned, whereby the collection locus in the housing is at the lower end of the housing, and water in the bore of the hollow fiber flows gravitationally downwardly to the collection locus.

191. A method according to claim 189, wherein each hollow fiber is coated on its exterior surface with a hydrophilicity-imparting agent.

192. A method according to claim 189, wherein each hollow fiber is formed of a material selected from the group consisting of polymeric materials, glasses and ceramics.

193. A method according to claim 189, wherein the hollow fiber has a porosity in a range suitable for application selected from the group consisting of ultrafiltration, microfiltration and reverse osmosis.

194. A method according to claim 189, wherein the hollow fiber has an outer diameter in the range of from about 100 micrometers to about 10 millimeters.

195. A method according to claim 189, wherein each hollow fiber is formed of a hydrophilic material.

196. A method of making an electrochemical cell module, comprising:

a multiplicity of microcells in an assembly comprising a multiplicity of component microcell sub-bundles,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

comprising fabricating the microcell assembly with a plurality of hollow fiber heat exchange elements arranged for flow of an aqueous coolant medium through a central lumen thereof, with the hollow fiber heat exchange elements being distributed in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module;

wherein said hollow fiber heat exchange elements comprise a water-permeable porous membrane separator, whereby water deriving from the aqueous coolant medium permeates from the bore through the membrane separator wall into the feed stream, thereby humidifying the electrochemical reaction environment.

197. The method of claim 196, further comprising mounting the assembly in a housing, and orienting same along an axis of the housing, potting a first end in a first potting member through which open ends of the microcell fibers are exposed for fluid flow therethrough, with the first potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first potting member, and further potting said heat exchange elements in a second potting member in spaced relationship to the first potting member, to define between the first and second potting members a closed volume of the housing, and providing a housing inlet communicating with the closed volume, for introduction of feed into the closed volume, for flow through the assembly on the bore side of the microcell fibers thereof, and wherein said second potting member defines with the housing a closed end volume, providing said heat exchange elements extending through the second potting member and terminating in the closed end volume at open ends of the heat exchange elements, and providing a coolant medium inlet communicating with the closed end volume, for introduction of aqueous coolant medium into the closed end volume, for flow of coolant axially through the heat exchange elements in the assembly;

potting a second end of the assembly in a first opposite potting member through which open opposite ends of the microcell fibers are exposed for fluid flow therethrough, with the first opposite potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first opposite potting member and said heat exchange elements further potted in a second opposite potting member in spaced relationship to the first opposite potting

member, to define between the first and second opposite potting members a closed opposite volume of the housing, and with a housing outlet communicating with the closed volume, for discharge of depleted fuel from the closed volume, and wherein said second opposite potting member defines with the housing a closed opposite end volume, with said heat exchange elements extending through the second opposite potting member and terminating in the closed opposite end volume at open ends of the heat exchange elements, and providing a coolant medium outlet communicating with the closed opposite end volume, for discharge of coolant medium from the closed opposite end volume, for removal of heat of electrochemical reaction from the assembly;

joining said current collectors at their ends in series or parallel with one another to form a terminal leak-tightly extending out of the housing; and

and leak-tightly joining a feed tube in feed communication with the shell side of the microcells in said assembly.

198. The method of claim 197, wherein each of the hollow fiber heat exchange elements is formed of a material comprising a water perm-selective agent.

199. The method of claim 197, wherein the water perm-selective agent comprises an ion-exchange fluoropolymer.

200. The method of claim 197, wherein the hollow fiber has a porosity in a range suitable for application selected from the group consisting of ultrafiltration, microfiltration and reverse osmosis.

201. The method of claim 197, wherein the hollow fiber has an outer diameter in the range of from about 100 micrometers to about 10 millimeters.
202. A coated fiber comprising a metal fiber formed of a material intrinsically susceptible to corrosion, and a continuous carbonaceous coating thereon of a pyrolyzed organic material, having a thickness imparting corrosion-resistance to the metal fiber:
203. A coated fiber according to claim 202, wherein said continuous coating of pyrolyzed organic material has an amorphous character.
204. A coated fiber according to claim 202, wherein said continuous coating of pyrolyzed organic material has a crystalline character.
205. A coated fiber according to claim 202, wherein said continuous carbonaceous coating has microporosity at its outer surface.
206. A coated fiber according to claim 202, wherein said continuous carbonaceous coating has a surface area of at least 10 meters<sup>2</sup> per gram of coating material, as measured by BET isotherm porosimetry.
207. A coated fiber according to claim 202, having a diameter in the range of from about 50 micrometers to about 10 millimeters.
208. A coated fiber according to claim 202, wherein said continuous carbonaceous coating comprises a vitreous glassy carbon material.

209. A coated fiber according to claim 202, further comprising an electrocatalyst on said continuous carbonaceous coating of pyrolyzed organic material.

210. A fibrous microcell structure comprising:

- an inner electrode,
- a microporous membrane separator in contact with the inner electrode,
- an electrolyte in pores of the microporous membrane separator,
- an outer electrode,

wherein at least one of the inner and outer electrodes includes a current collector comprising a coated fiber including a metal fiber formed of a material intrinsically susceptible to corrosion, and a continuous carbonaceous coating thereon of a pyrolyzed organic material, having a thickness imparting corrosion-resistance to the metal fiber.

211. An electrochemical cell device, including a plurality of fibrous microcell structures as in claim 210.

212. An electrochemical cell device according to claim 211, constituting a fuel cell.

213. An electrochemical cell device according to claim 211, constituting a battery cell.

214. An electrochemical device comprising a current collector formed of a corrosion-susceptible metal with a continuous carbonaceous coating thereon of a pyrolyzed organic material, having a thickness imparting corrosion-resistance to the metal current collector.

215. An electrochemical device according to claim 214, constituting a fuel cell.
216. An electrochemical device according to claim 214, constituting a battery cell.
217. An electrochemical device according to claim 214, wherein said current collector has a plate conformation.
218. An electrochemical device according to claim 214, wherein said current collector has a fibrous conformation.
219. An electrochemical device according to claim 214, wherein said current collector is of sheet or web form.
220. An electrochemical device according to claim 214, wherein said continuous carbonaceous coating has an amorphous character.
221. An electrochemical device according to claim 214, wherein said continuous carbonaceous coating has a crystalline character.
222. An electrochemical device according to claim 214, wherein said continuous carbonaceous coating has a vitreous glassy carbon character.
223. A fuel cell comprising microcell fibrous elements including a current collector or an electrode coated with an amorphous metal composition.



224. A fuel cell comprising microcell fibrous elements including a current collector or an electrode coated with a metal composition having hydrogen storage capability.

225. A microcell structure comprising:

- an inner electrode,
- a microporous membrane separator in contact with the inner electrode,
- an electrolyte in pores of the microporous membrane separator,
- an outer electrode,

wherein at least one of the inner and outer electrodes includes a carbon or graphitic current collector in intimate contact with a non-carbon or non-graphitic current collector susceptible to degradation producing electrical discontinuity thereof.

226. A electrochemical cell comprising a plurality of microcell structures as in claim 225.

227. A method of fabricating a corrosion-resistant fiber, comprising:

- providing a metal fiber formed a material intrinsically susceptible to corrosion;
- applying to said fiber a coating of an organic material having a thickness providing a pyrolysis product imparting corrosion-resistance to the metal fiber;
- pyrolyzing said organic material on said fiber to form a continuous carbonaceous coating thereon.

228. The method according to claim 227, wherein said continuous coating of pyrolyzed organic material has an amorphous character.

229. The method according to claim 227, wherein said continuous coating of pyrolyzed organic material has a crystalline character.
230. The method according to claim 227, wherein said continuous carbonaceous coating has microporosity at its outer surface.
231. The method according to claim 227, wherein said continuous carbonaceous coating has a surface area of at least 10 meters<sup>2</sup> per gram of coating material, as measured by BET isotherm porosimetry.
232. The method according to claim 227, wherein the coated fiber has a diameter in the range of from about 50 micrometers to about 10 millimeters.
233. The method according to claim 227, wherein said continuous carbonaceous coating comprises a vitreous glassy carbon material.
234. The method according to claim 227, further comprising forming an electrocatalyst on said continuous carbonaceous coating of pyrolyzed organic material.
235. A method of making a fibrous microcell structure comprising:
- an inner electrode,
  - a microporous membrane separator in contact with the inner electrode,
  - an electrolyte in pores of the microporous membrane separator,
  - an outer electrode,

wherein at least one of the inner and outer electrodes includes a current collector, said method comprising forming said current collector as a coated fiber including a metal fiber formed of a material intrinsically susceptible to corrosion, and a continuous carbonaceous coating thereon of a pyrolyzed organic material, having a thickness imparting corrosion-resistance to the metal fiber.

236. A method of fabricating an electrochemical device comprising forming a current collector of a corrosion-susceptible metal and coating a continuous carbonaceous coating thereon of a pyrolyzed organic material, having a thickness imparting corrosion-resistance to the metal current collector.

237. The method of claim 236, wherein said electrochemical device constitutes a fuel cell.

238. The method of claim 236, wherein said electrochemical device constitutes a battery cell.

239. The method of claim 236, wherein said electrochemical device constitutes a current collector having a plate conformation.

240. The method of claim 236, wherein said electrochemical device constitutes a current collector having a fibrous conformation.

241. The method of claim 240, wherein said electrochemical device constitutes a current collector having a sheet or web form.

242. The method of claim 236, wherein said continuous carbonaceous coating has an amorphous character.

243. The method of claim 236, wherein said continuous carbonaceous coating has a crystalline character.

244. The method of claim 236, wherein said continuous carbonaceous coating has a vitreous glassy carbon character.

245. The method of claim 236, wherein said current collector or an electrode is coated with an amorphous metal composition.

246. A method of fabricating a fuel cell comprising coating microcell fibrous elements including a current collector or an electrode coated with a metal composition having hydrogen storage capability.

247. A method of fabricating a microcell structure comprising:

- an inner electrode,
- a microporous membrane separator in contact with the inner electrode,
- an electrolyte in pores of the microporous membrane separator,
- an outer electrode,

comprising providing as at least one of the inner and outer electrodes, a carbon or graphitic current collector in intimate contact with a non-carbon or non-graphitic current collector susceptible to degradation producing electrical discontinuity thereof.

**AMENDED CLAIMS**

[received by the International Bureau on 17 December 2001(17.12.01);  
original claims 1, 7, 10-11, 13-14, 27, 31, 33, 36-37, 40, 42, 84, 106, 110, 113-114, 126-128,  
130, 133-134, 137, 140-141, 146, 148, 153-155, 159, 175-176, 214 and 217-219  
amended; claims 9, 35, 183-188 and 196-201 cancelled;  
remaining claims unchanged (30 pages)]

**+ STATEMENT**

1. A microcell assembly, wherein each microcell comprises:

an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

said assembly comprising a first cell including a first microcell sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, with each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member;

an insulating sheet for electrical isolation of the first cell from a further cell overlying the insulating sheet;

a second cell including a first microcell sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from one edge of the second sheet member, adjacent the second edge of the first sheet

6. The microcell module of claim 5, circumscribingly enclosed in said shell and tube structural arrangement.
7. A microcell sub-bundle article, comprising:

a sheet assembly including: (a) a first microcell sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said microcell fibers axially extending from a first edge of a first sheet member, (b) a second sheet member of external current collectors overlying the first sheet member, with each current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member, (c) a porous, electrically insulative sheet member overlying the second sheet member, (d) a third sheet member comprising a plurality of microcell fibers parallelly arranged and interconnected in a substantially planar conformation, with inner current collector of said microcell fibers axially extending from a first edge of said third sheet member, and (e) a fourth sheet member of external current collectors overlying the third sheet member, with each current collector of the fourth sheet member in contact with at least one microcell fiber of the third sheet member and extending beyond an opposite, second edge of the fourth sheet member,

wherein the inner current collectors of the first and third sheet members are generally coextensive in length with one another at their ends, and the external current collectors of the second and the fourth sheet members are generally coextensive in length with one another at their ends, and wherein said ends of the external current

collectors of the second sheet member and the inner current collectors of the third sheet member are electrically connected at their ends;

wherein the sub-bundle has been formed by axially rolling the sheet assembly into a cylindrical pre-form, applying a porous and electrically insulative wrap to the outer cylindrical surface of the cylindrical pre-form; and potting at respective ends of the cylindrical pre-form, to yield said sub-bundle,

wherein the first and second sheet members form a first cell, and the third and fourth sheet members form a second cell, and wherein the first cell and second cell form a serial connection.

8. A microcell sub-bundle article according to claim 7, further comprising a central tubular member that is perforate over an intermediate length thereof between the potted ends, and otherwise imperforate outside of the potted ends.
10. A microcell sub-bundle article according to claim 7, comprising a plurality of microcell fiber sheets and external current collector sheets forming multiple cells in serial connection.
11. A microcell sub-bundle article according to claim 7, wherein the article comprises a repeating sequence of microcell fiber sheets and external current collector sheet members forming a multiplicity of cells, wherein each cell is separated from an adjacent cell by a porous, electrically insulative sheet member, and each cell is electrically connected to adjacent cells by serial connection.
12. A series-connected assembly of at least two sub-bundles as in claim 7.

13. A microcell article comprising a series of microcell sub-bundle articles as in claim 7, sequentially connected in positive-to-negative electrode arrangement, having an elongate character.
14. A microcell article as in claim 13, wherein each two adjacent microcell sub-bundle articles are serially connected by a flexible connector, said connector comprising a pair of crimpable conductive leaves that are spaced apart and interconnected by a flexible conductive yoke element, and wherein each crimpable conductive leaf compressively grip a protuberant group of current collectors of a sub-bundle.
15. The microcell article of claim 13, wherein the connection comprises welding, brazing, soldering, conductive adhesive bonding, or melt bonding.
16. A microcell article comprising a series of microcell sub-bundle articles as in claim 11, sequentially connected in positive-to-negative electrode arrangement, in a bundle wherein component sub-bundle articles are parallelly aligned with one another in side-by-side relationship of consecutive sub-bundle articles, and the bundle has an axial dimension that substantially equal to the axial dimension of each sub-bundle article in the bundle.
17. The microcell article of claim 16, wherein the bundle is potted at respective ends.
18. A microcell article, comprising a plurality of microcell sub-bundle articles as in claim 11, arranged in side-by-side relationship, with electrodes of adjacent ones of said sub-bundle articles being electrically interconnected in positive-to-negative electrode relationship, and with the microcell article being potted at respective ends thereof.



shaping said multilayer structure into a predetermined sub-bundle shape, and potting same to impart a permanent shape thereto, wherein said permanent shape provides localized conformations of internal and external current collectors;

fabricating a plurality of sub-bundles in corresponding manner;

connecting said sub-bundles in sequence to form a series arrangement of sub-bundles; and

shaping the series-connected sub-bundles to form a bundle assembly.

27. A method of fabricating a microcell assembly, comprising:

forming a first layer including a first microcell sheet member comprising a plurality of fibrous microcell elements parallelly arranged and interconnected in a substantially planar conformation, with inner current collectors of said fibrous microcell elements axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, positioning each external current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member;

disposing an insulating sheet on said first layer;

forming a second layer including a first microcell sheet member comprising a plurality of fibrous microcell elements parallelly arranged and interconnected

in a substantially planar conformation, with inner current collectors of said fibrous microcell elements axially extending from a first edge of a first sheet member, and a second sheet member of external current collectors overlying the first sheet member, positioning each external current collector in contact with at least one microcell fiber of the first sheet member and extending beyond an opposite, second edge of the first sheet member; and

electrically connecting the inner current collectors of the first layer with the external current collectors of the second layer to form a series connection therewith.

28. The method of claim 27, wherein the current collectors are interconnected by soldering, brazing, welding, conductive adhesive bonding, or melt bonding.
29. The method of claim 27, comprising forming an assembly comprising a multiplicity of said first and second layers in alternating sequence, and electrically interconnecting successive layers in series relationship to one another.
30. The method of claim 27, further comprising potting the microcell assembly to seal the shell side and bore side of the fibrous microcell elements from one another
31. A method of fabricating a microcell module, comprising:

providing a gas feed chamber including a perforate plate member;

positioning on the perforated plate member at least one microcell assembly of claim 1, and

potting the microcell assembly at respective ends thereof by potting members forming respective seal faces which when the seal faces at their periphery are abuttingly reposed in a housing, form a shell and tube structural arrangement, wherein the perforated plate member is intermediately positioned between the potting members.

32. A method according to claim 31, comprising circumscribingly enclosing the microcell module in a housing to form said shell and tube structural arrangement.

33. A method of fabricating a microcell sub-bundle article, comprising:

forming a sheet assembly of claim 1;

axially rolling the sheet assembly into a cylindrical pre-form, applying a porous and electrically insulative wrap to the outer cylindrical surface of the cylindrical pre-form; and potting respective ends of the cylindrical pre-form, to yield said sub-bundle.

34. A method according to claim 33, wherein the sheet assembly is rolled on a central tubular member that is perforate over an intermediate length thereof between the potted ends, and otherwise imperforate outside of the potted ends.

36. A method according to claim 34, comprising fabricating the microcell sub-bundle article with a plurality of microcell fiber sheets and external current collector sheets forming multiple cells in serial connection.

37. A method according to claim 34, comprising fabricating a repeating sequence of microcell fiber sheets and external current collector sheet members forming a

multiplicity of cells in serial connection, and disposing a porous, electrically insulative sheet between successive cells.

38. A method according to claim 34, comprising electrically connecting at least two sub-bundles in series.
39. A method according to claim 38, wherein said at least two sub-bundles are sequentially connected in positive-to-negative electrode arrangement, having an elongate character.
40. A method according to claim 38, wherein said step of electrically connecting at least two sub-bundles in series, comprises interconnecting successive sub-bundles with a flexible connector, said connector comprising a pair of crimpable conductive leaves that are spaced apart and interconnected by a flexible conductive yoke element, and wherein each crimpable conductive leaf compressively grip a protuberant group of current collectors of a sub-bundle.
41. A method according to claim 38, wherein said step of electrically connecting at least two sub-bundles in series, comprises welding, brazing, soldering, conductive adhesive bonding, or melt bonding.
42. A method of fabricating a microcell article comprising a series of microcell sub-bundle articles, said method including fabricating a plurality of microcell sub-bundle articles of claim 7, parallelly aligning said sub-bundle articles with one another in side-by-side relationship of consecutive sub-bundle articles, thereby forming a bundle of said sub-bundle articles, and electrically interconnecting the sub-bundle articles in series.

81. The method of claim 78, wherein the fibrous microcell structure has an outer diameter in the range of from about 100 microns to about 10 millimeters.
82. The method of claim 78, wherein the permselective membrane is applied to the porous membrane separator by a method selected from the group consisting of electroless plating, electrochemical deposition, extrusion, vapor deposition, solution deposition.
83. The method of claim 78, wherein the permselective membrane comprises a material selected from the group consisting of metals and electrically conductive polymeric materials.
84. The method of claim 78, wherein the permselective membrane comprises palladium.
85. The method of claim 80, wherein the hydrophobicity-imparting material comprises a fluoropolymer.
86. The method of claim 80, wherein the hydrophobicity-imparting material comprises polytetrafluoroethylene.
87. A method of making a fibrous microcell structure comprising providing an inner porous membrane separator bounding a central lumen and coating, impregnating or extruding at an inner surface thereof a hydrogen- or oxygen-permselective membrane thereon, and disposing a first electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface thereof, to thereby form an interior structure, encapsulating the interior structure with an outer porous membrane separator, placing a second electrocatalyst material and at least one electrically conductive fiber in contact with an outer surface of the outer porous membrane

102. The method according to claim 101, wherein the reformer catalyst comprises a metal oxide.
103. The method according to claim 101, wherein the reformer catalyst comprises a metal oxide selected from the group consisting of copper oxide, zinc oxide and mixtures thereof.
104. The method according to claim 101, wherein the reformer catalyst is catalytically effective to convert CO to CO<sub>2</sub>.
105. The method according to claim 101, wherein the porous membrane separator is formed of a material selected from the group consisting of glasses, ceramics and polymeric materials.
106. A process system comprising:

a supply of microcell precursor comprising at least one current collector within a porous membrane separator arranged in dispensing relationship;

a liquid contacting unit arranged for receiving microcell precursor from said supply, wherein dispensed microcell precursor is contacted with an electrocatalyst and at least one of electrocatalyst reducing agent and hydrophobicity-imparting material;

optionally a dryer unit arranged for receiving microcell precursor from the liquid contacting unit for drying the microcell precursor; and

collection means for collecting the precursor after liquid contacting and optional drying thereof.

107. A process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an ion exchange polymer solution.
108. A process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst solution.
109. A process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst reducing solution.
110. A process system, comprising:
- a supply of microcell precursor comprising at least one current collector within a porous membrane separator arranged in dispensing relationship;
  - a liquid contacting unit arranged for receiving microcell precursor from said supply, wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst solution comprising platinic acid solution;
  - optionally a dryer unit arranged for receiving microcell precursor from the liquid contacting unit for drying the microcell precursor; and
  - collection means for collecting the precursor after liquid contacting and optional drying thereof.

111. The process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an electrocatalyst reducing agent comprising sodium borohydride.
112. The process system according to claim 106 wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with a hydrophobicity-imparting material comprising a PTFE emulsion.
113. A process system, comprising:
- a supply of microcell precursor comprising at least one current collector within a porous membrane separator arranged in dispensing relationship;
- a liquid contacting unit arranged for receiving microcell precursor from said supply, wherein the liquid contacting unit comprises a liquid bath for contacting the precursor with an ink solution comprising an electrocatalyst, carbon powder, ion exchange polymer, and a hydrophobicity-imparting material;
- optionally a dryer unit arranged for receiving microcell precursor from the liquid contacting unit for drying the microcell precursor; and
- collection means for collecting the precursor after liquid contacting and optional drying thereof.
114. A process for manufacturing a fiber microcell article, comprising the steps of:
- disposing electrolyte material in pores of a microcell precursor article;
- drying the precursor article;
- applying electrocatalyst material in the form of solution or ink slurry to the precursor;



drying the precursor article;

reducing the electrocatalyst material to a catalytically active form, using an electrocatalyst reducing solution.

115. The process according to claim 114, wherein the electrocatalyst material comprises an ink slurry and said slurry is applied to the precursor article by extrusion.

116. The process according to claim 114, wherein the microcell precursor article is formed by passage of a strand or tow of a fibrous current collector through the bore-forming tube of a hollow fiber extrusion mold with gaseous or liquid coagulants.

117. The process according to claim 114, wherein the microcell precursor article is formed by the steps of:

providing a fiber or tow of current collector(s);

applying to said fiber or tow a porous membrane-forming material;

processing the fiber or tow having the porous membrane-forming material thereon, to form porosity therein.

118. The process according to claim 117, wherein the porous membrane-forming material has porosity in a range suitable for application selected from the group consisting of ultrafiltration, microfiltration and reverse osmosis.

119. The process according to claim 117, wherein the porous membrane-forming material is formed from a material selected from the group consisting of polymeric materials, glasses, ceramics, and combinations thereof.

120. The process according to claim 117, wherein the porous membrane-forming material is applied by a method selected from the group consisting of wet spinning and melt spinning.
121. The process according to claim 117, wherein the porous membrane-forming material comprises a dope including a backbone component and a leachable component that upon removal by leaching yields voids constituting porosity of the porous membrane.
122. The process according to claim 117, wherein the porous membrane-forming material comprises a dope, and wherein a coagulating agent is applied to the dope on at least one of an inner surface and outer surface of the applied dope.
123. The process according to claim 117, wherein the porous membrane-forming material is applied by melt-spinning and wherein the fiber or tow having the melt-spinning material applied thereto is contacted with a quench medium.
124. The process according to claim 122, wherein an electrocatalyst ink paste is coextruded with the coagulating agent on said inner surface.
125. The process according to claim 117, further comprising the steps of:
  - coating the porous membrane separator with one of a perm-selective membrane material and an ion-exchange polymer.
126. The process according to claim 117, further comprising fabricating a microcell module comprising a plurality of the precursor articles wherein the precursor articles are potted and sealed to form a shell-and-bore conformation with precursor articles aligned parallelly with one another, and flowing through at least one of the shell side

and the bore side of said shell-and-bore conformation an electrocatalyst solution, electrocatalyst ink or a reducing agent.

127. The process according to claim 117, further comprising fabricating a microcell module comprising a plurality of the precursor articles wherein the precursor articles are potted and sealed to form a shell-and-bore conformation with precursor articles aligned parallelly with one another, and electrocatalyst material is applied to at one of the shell side and the bore side of said shell-and-bore conformation in situ.

128. The process according to claim 127 wherein the electrocatalyst material is applied to the shell-and-bore conformation by a method selected from the group consisting of electroless plating, electrochemical deposition, extrusion, vapor deposition, solution deposition.

129. The process of claim 117 wherein the membrane separator comprises a membrane selected from the group consisting of semi-permeable membranes and ion exchange membranes.

130. An electrochemical cell module, comprising:  
a multiplicity of microcells in an assembly,  
each microcell comprising an inner electrode,  
a microporous membrane separator in contact with the inner electrode,  
an electrolyte in pores of the microporous membrane separator,  
an outer electrode,  
with the microcell assembly including a plurality of hollow, nonporous tubular heat exchange elements arranged for flow of a coolant medium through a central lumen thereof, with the hollow, nonporous tubular heat exchange elements being distributed

in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module;

a source of said coolant medium; and  
flow circuitry interconnecting the source of said coolant medium and said hollow, nonporous tubular heat exchange elements.

131. The electrochemical cell module of claim 130, wherein said coolant medium is a liquid coolant.
132. The electrochemical cell module of claim 130, wherein said coolant medium is a gas.
133. The electrochemical cell module of claim 130, wherein said flow circuitry comprises a manifold at each of opposite ends of said assembly of microcells, and said hollow, nonporous tubular heat exchange elements are coupled in flow communication at opposite ends thereof with a corresponding manifold, and a pump joined to said flow circuitry for effecting flow of said coolant medium through the hollow, nonporous tubular heat exchange elements in the module, to remove heat generated by said assembly by electrochemical reaction in the microcells.
134. The electrochemical cell module of claim 130, wherein the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a first potting member through which open ends of the microcell fibers are exposed for fluid flow therethrough, with the first potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first potting member, and said hollow, nonporous tubular heat exchange elements further potted in a second potting member in spaced relationship to the first potting member, to define between the first and second potting members a closed volume of the housing, and with a housing inlet communicating with the closed

volume, for introduction of feed into the closed volume, for flow through the assembly on the bore side of the microcell fibers thereof, and wherein said second potting member defines with the housing a closed end volume, with said hollow, nonporous tubular heat exchange elements extending through the second potting member and terminating in the closed end volume at open ends of the heat exchange elements, and with a coolant medium inlet communicating with the closed end volume, for introduction of coolant medium into the closed end volume, for flow of coolant axially through the tubular heat exchange elements in the assembly;

with a second end of the assembly potted in a first opposite potting member through which open opposite ends of the microcell fibers are exposed for fluid flow therethrough, with the first opposite potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first opposite potting member, and said hollow, nonporous tubular heat exchange elements further potted in a second opposite potting member in spaced relationship to the first opposite potting member, to define between the first and second opposite potting members a closed opposite volume of the housing, and with a housing outlet communicating with the closed volume, for discharge of depleted fuel from the closed volume, and wherein said second opposite potting member defines with the housing a closed opposite end volume, with said hollow, nonporous tubular heat exchange elements extending through the second opposite potting member and terminating in the closed opposite end volume at open ends of the heat exchange elements, and with a coolant medium outlet communicating with the closed opposite end volume, for discharge of coolant medium from the closed opposite end volume, for removal of heat of electrochemical reaction from the assembly;

wherein said current collectors at their ends are joined in series or parallel with one another to form a terminal leak-tightly extending out of the housing;

and a feed tube leak-tightly joined in feed communication with the shell side of the microcells in said assembly.

135. The electrochemical cell module of claim 133, wherein the feed tube extends axially into the housing, and through the first and second potting members.
136. The electrochemical cell module of claim 133, wherein the current collectors extending axially of the first potting member are either bore-side current collectors or shell-side current collectors, and the current collectors extending axially of the first opposite potting member are either shell-side current collectors or bore-side current collectors, opposite to that of the current collectors extending axially of the first potting member.
137. The electrochemical cell module of claim 133, wherein each of said current collectors at an opposite end thereof either (a) terminates in a corresponding closed volume between a first and second potting member, and is distinct from said hollow, nonporous tubular heat exchange elements or (b) terminates in an end volume, and is a said hollow, nonporous tubular heat exchange element, and
- wherein each of said current collectors at an opposite end thereof is connected in series or parallel with ends of other current collectors to form a terminal leak-tightly extending out of the housing.
138. The electrochemical cell module of claim 133, further comprising (i) an oxidant inlet communicating with the assembly in the housing for flow of oxidant on one of the shell side and bore side of the microcell fibers in the assembly, opposite to the side

receiving feed, and (ii) a spent oxidant outlet communicating with the assembly in the housing for flow of spent oxidant out of the housing.

139. The electrochemical cell module of claim 133, wherein the housing comprises separable assembly accommodating removal of a separable part thereof to access an interior volume and components of the module.
140. The electrochemical cell module of claim 133, wherein the hollow, nonporous heat exchange elements have a cross-sectional diameter of from about 100 microns to about 10 centimeters.
141. The electrochemical cell module of claim 133, wherein the hollow, nonporous heat exchange elements and the current collectors are separate and distinct elements.
142. An electrochemical cell module, comprising:
- a multiplicity of microcells in an assembly,
  - each microcell comprising an inner electrode,
  - a microporous membrane separator in contact with the inner electrode,
  - an electrolyte in pores of the microporous membrane separator, and
  - an outer electrode,

wherein the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a first potting member through which open ends of

microcell fibers from the bore side thereof to form a closed end volume isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors constituting heat exchange elements and extending axially of the opposite potting member into the closed end volume, and coupled to at least one second heat exchange passage in the housing, with said at least one second heat exchange passage being arranged for flow of a coolant medium therethrough, and with a housing outlet communicating with the closed end volume, for discharge of depleted fuel from the closed end volume;

and wherein said current collectors at their ends are joined in series or parallel with one another to form a terminal leak-tightly extending out of the housing.

144. The electrochemical cell module of claim 142, wherein the first and second heat exchange passages are interconnected with one another.
145. The electrochemical cell module of claim 142, wherein the assembly comprises a multiplicity of component microcell sub-bundles and said sub-bundles are joined in series arrangement with one another in said array.
146. The electrochemical cell module of claim 130, wherein the hollow, nonporous tubular heat exchange elements are distributed between microcell sub-bundles as intra-sub-bundle heat exchange elements.
147. An electrochemical cell module, comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode active material,



a microporous membrane separator in contact with the inner electrode active element,

an electrolyte in pores of the microporous membrane separator,

an outer electrode active element,

with each of the inner and outer electrode active elements comprising at least one of electrode, current collector and electrocatalyst components, and said assembly including electrode or current collector components extending externally of the assembly to end portions thereof;

wherein the assembly is contained in a housing including a coolant reservoir;

a coolant in the coolant reservoir; and

said end portions of said electrode or current collector components being coupled in solid heat conduction relationship with said coolant, to enable solid conduction transfer of heat from said assembly of microcells through said electrode or current collector components to the coolant, to thereby remove heat generated by electrochemical reaction in said microcells during operation of the module.

148. The electrochemical cell module of claim 142, wherein said current collectors constituting heat exchange elements are hollow, nonporous, electrically and thermally conductive tubes formed of a material of construction selected from the group consisting of metals, metals coated with corrosion resistant material, graphite and polymeric materials.

149. The electrochemical cell module of claim 142, wherein said microcells have a size of from about 100 microns to about 10 mm.
150. The electrochemical cell module of claim 142, wherein said microcells have a size of from about 100 microns to about 10 mm.
151. The electrochemical cell module of claim 142, wherein the coolant medium is a gas or liquid.
152. The electrochemical cell module of claim 142, wherein said potting members are formed of a material of construction selected from the group consisting of epoxy, polyurethane, bismaleimide, rubber, and elastomer materials.
153. A microcell module comprising an assembly of microcells wherein each microcell includes:
- an inner electrode active material,
  - a microporous membrane separator in contact with the inner electrode active element,
  - an electrolyte in pores of the microporous membrane separator, and
  - an outer electrode active element,

with each of the inner and outer electrode active elements comprising at least one of electrode, current collector and electrocatalyst components, and said microcell including an elongate electrode or current collector;

means for extracting heat from the assembly selected from the group consisting of:

- (a) hollow, nonporous tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements do not constitute current collectors;
- (b) hollow, nonporous tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements constitute current collectors; and
- (c) solid current collectors extending from the assembly of microcells and coupled in heat exchange relationship with a coolant medium.

154. A process for generating electrochemical energy, comprising:

(A) providing an electrochemical cell module, comprising:

a multiplicity of microcells in an assembly,

each microcell comprising an inner electrode,

a microporous membrane separator in contact with the inner electrode,

an electrolyte in pores of the microporous membrane separator,

an outer electrode,

with the microcell assembly including a plurality of hollow, nonporous tubular heat exchange elements arranged for flow of a coolant medium through a central lumen thereof, with the hollow, nonporous tubular heat exchange elements being distributed in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module;

a source of said coolant medium;

flow circuitry interconnecting the source of said coolant medium and said hollow, nonporous tubular heat exchange elements;

(B) providing fuel to the electrochemical cell module to one of the shell side and bore side of the microcells in said assembly;

(C) concurrently providing oxidant to the electrochemical cell module to the opposite one of the shell side and bore side of the microcells in said assembly, relative to the side receiving fuel, and thereby effecting electrochemical reaction to generate electrical energy and heat;

(D) discharging depleted feed from the electrochemical cell module;

(E) flowing said coolant medium from said source of same through said flow circuitry and said hollow, nonporous tubular heat exchange elements to remove heat from the electrochemical cell module;

(F) discharging said coolant medium from the module.

155. A process according to claim 154, further comprising the steps of:

(G) flowing the discharged coolant medium through a heat exchanger to remove sensible heat therefrom and yield coolant medium of lower temperature; and

(H) recirculating the lower temperature coolant medium to the module for flow through the hollow, nonporous tubular heat exchange elements.

156. A process according to claim 154, wherein the coolant medium comprises water.
157. A process according to claim 154, wherein the coolant medium comprises an aqueous glycol solution.
158. A process according to claim 154, wherein at least one of the shell and tube sides is at superatmospheric pressure.
159. A method of thermally managing operation of an electrochemical cell module comprising:
- a multiplicity of microcells in an assembly,
  - each microcell comprising an inner electrode,
  - a microporous membrane separator in contact with the inner electrode,
  - an electrolyte in pores of the microporous membrane separator,
  - an outer electrode,
- said method comprising disposing in the microcell assembly a plurality of hollow, nonporous fiber heat exchange elements arranged for flow of a coolant medium through a central lumen thereof, with the hollow, nonporous fiber heat exchange elements being distributed in said assembly for heat removal from the assembly during electrochemical reaction in operation of the module; and

flowing a coolant medium through said hollow, nonporous fiber heat exchange elements during electrochemical reaction in the microcell assembly.

160. The method of claim 159, wherein said coolant medium is a liquid coolant.

161. The method of claim 159, wherein said coolant medium is a gas.

162. The method of claim 159, wherein:

the assembly is mounted in a housing, and oriented along an axis of the housing, with a first end potted in a first potting member through which open ends of the microcell fibers are exposed for fluid flow therethrough, with the first potting member isolating the shell side of the microcell fibers from the bore side thereof, and with current collectors extending axially of the first potting member, a second potting member in spaced relationship to the first potting member, to define between the first and second potting members a closed volume of the housing, and with a housing inlet communicating with the closed volume, for introduction of feed into the closed volume, for flow through the assembly on the bore side of the microcell elements thereof, and wherein said second potting member defines with the housing a closed end volume, with said heat exchange elements extending through the second potting member and terminating in the closed end volume at open ends of the heat exchange elements, and with a coolant medium inlet communicating with the closed end volume, for introduction of coolant medium into the closed end volume, for flow of coolant axially through the heat exchange elements in the assembly;

a second end of the assembly is potted in a first opposite potting member through which open opposite ends of the microcell elements are exposed for fluid flow therethrough, with the first opposite potting member isolating the shell side of the microcell elements from the bore side thereof, and with current collectors extending

mounting the assembly in a housing including a coolant reservoir with the end portions of said electrode or current collector components positioned in the reservoir; and

providing a coolant in the coolant reservoir to immerse the end portions of the electrode or current collector elements in the coolant, to enable solid conduction transfer of heat from said assembly of microcells through said electrode or current collector components to the coolant, to thereby remove heat generated by electrochemical reaction in said microcells during operation of the module.

175. A method of thermal management of a microcell module comprising an assembly of microcells wherein each microcell includes:

an inner electrode active material,

a microporous membrane separator in contact with the inner electrode active element,

an electrolyte in pores of the microporous membrane separator, and

an outer electrode active element,

with each of the inner and outer electrode active elements comprising at least one of electrode, current collector and electrocatalyst components, and said microcell including an elongate electrode or current collector;

said method comprising extracting heat from the assembly by use of a means selected from the group consisting of:

- (a) hollow, nonporous tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements do not constitute current collectors;
- (b) hollow, nonporous tubular heat exchange elements extending through the assembly of microcells, wherein said tubular heat exchange elements constitute current collectors; and
- (c) solid current collectors extending from the assembly of microcells and coupled in heat exchange relationship with a coolant medium.

176. An electrochemical device comprising water-permeable membrane hollow fibers distributed in an assembly including a plurality of microcells potted at respective ends of the assembly and disposed within a housing wherein the potted respective ends bound an interior volume therebetween, and wherein the hollow fibers are parallelly aligned with microcells of the assembly, with each hollow fiber having a first open end extending through the tubesheet exteriorly of the interior volume and the other end terminating at or before the opposite potting member, whereby the hollow fibers are arranged to absorb water produced in the electrochemical reaction by wicking action and channeling water away from the locus of electrochemical reaction by permeation through the wall of the hollow fiber and flow thereof through the bore of the hollow fiber to a collection locus in the housing outside of the interior volume.

177. An electrochemical device according to claim 176, wherein the housing is oriented so that the microcell elements and the hollow fibers are vertically aligned, whereby the collection locus in the housing is at the lower end of the housing, and water in the bore of the hollow fiber flows gravitationally downwardly to the collection locus.



susceptible to corrosion, and a continuous carbonaceous coating thereon of a pyrolyzed organic material, having a thickness imparting corrosion-resistance to the metal fiber.

- 211. An electrochemical cell device, including a plurality of fibrous microcell structures as in claim 210.
- 212. An electrochemical cell device according to claim 211, constituting a fuel cell.
- 213. An electrochemical cell device according to claim 211, constituting a battery cell.
- 214. An electrochemical device comprising a carbon or graphitic current collector in intimate contact with a coated metal current collector formed of a corrosion-susceptible metal with a continuous carbonaceous coating thereon of a pyrolyzed organic material, having a thickness imparting corrosion-resistance to the metal current collector.
- 215. An electrochemical device according to claim 214, constituting a fuel cell.
- 216. An electrochemical device according to claim 214, constituting a battery cell.
- 217. An electrochemical device according to claim 214, wherein said coated metal current collector has a plate conformation.
- 218. An electrochemical device according to claim 214, wherein said coated metal current collector has a fibrous conformation.

219. An electrochemical device according to claim 214, wherein said coated metal current collector is of sheet or web form.
220. An electrochemical device according to claim 214, wherein said continuous carbonaceous coating has an amorphous character.
221. An electrochemical device according to claim 214, wherein said continuous carbonaceous coating has a crystalline character.
222. An electrochemical device according to claim 214, wherein said continuous carbonaceous coating has a vitreous glassy carbon character.
223. A fuel cell comprising microcell fibrous elements including a current collector or an electrode coated with an amorphous metal composition.
224. A fuel cell comprising microcell fibrous elements including a current collector or an electrode coated with a metal composition having hydrogen storage capability.
225. A microcell structure comprising:
- an inner electrode,
  - a microporous membrane separator in contact with the inner electrode,
  - an electrolyte in pores of the microporous membrane separator,
  - an outer electrode,
- wherein at least one of the inner and outer electrodes includes a carbon or graphitic current collector in intimate contact with a non-carbon or non-graphitic current collector susceptible to degradation producing electrical discontinuity thereof.

Please replace pages 59-118 of the application as filed, with the enclosed new substitute pages 59-111.

**§205(b) Statement**

In the new pages of claims, the differences between the claims as originally filed in the application, and the claims as amended by the substitute pages 59-111 accompanying the Article 19 Statement, are summarized below:

Claims 9, 35, 183-188, 196-201 have been cancelled.

Claims 1, 7, 10-11, 13-14, 27, 31, 33, 36-37, 40, 42, 84, 106, 110, 113-114, 126-128, 130, 133-134, 137, 140-141, 146, 148, 153-155, 159, 175-176, 214, and 217-219 have been amended.

Remaining claims 2-6, 8, 12, 15-26, 28-30, 32, 34, 38-39, 41, 43-83, 85-105, 107-109, 111-112, 115-125, 129, 131-132, 135-136, 138-139, 142-145, 147, 149-152, 156-158, 160-174, 177-182, 189-195, 202-213, 215-216, 220-247 have been retained unchanged.

Specifically, claims 1 and 176 have been amended to correct misspelling of the word "parallelly".

Claim 7 has been amended to incorporate the limitations of claim 9.

Claims 10 and 11 have been amended to reflect the changes made to claim 7.

Claim 13 has been amended to depend from claim 7 instead of claim 11.

Claims 14 and 40 have been amended to further define the structure of the connector for connecting the microcell sub-bundles.

Claims 31 and 33 have been amended to depend from claim 1.

Claims 36 and 37 have been amended to reflect the changes made to their base claim 33, upon which claims 36 and 37 indirectly depend.

Claim 42 has been amended to depend from claim 7.

Claim 84 has been amended to depend from claim 78 instead of claim 87.

Claim 106 has been amended to require that the dispensed microcell precursor be contacted with "an electrocatalyst and at least one of an electrocatalyst reducing agent and hydrophobicity-imparting material".

Claims 110 and 113 have been rewritten into independent form.

Claim 114 has been amended so that it requires the step of "reducing the electrocatalyst material to a catalytically active form, using an electrocatalyst reducing solution."

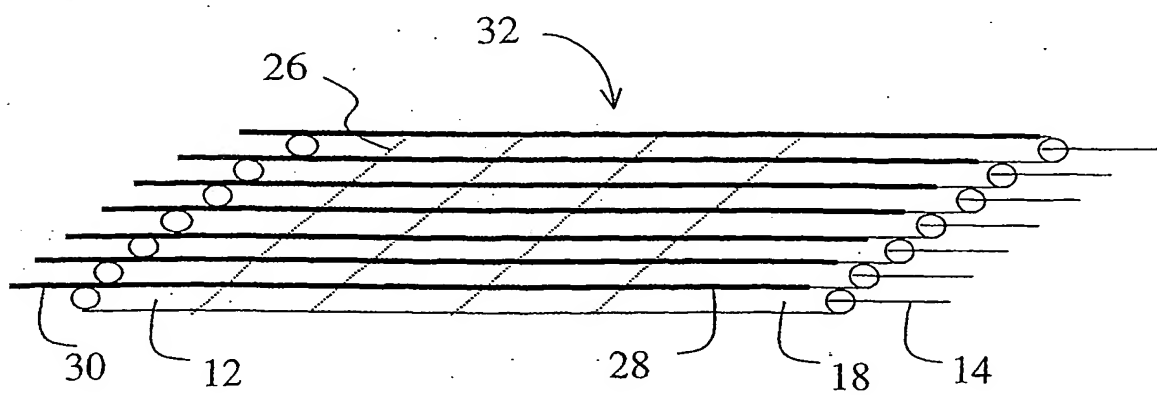
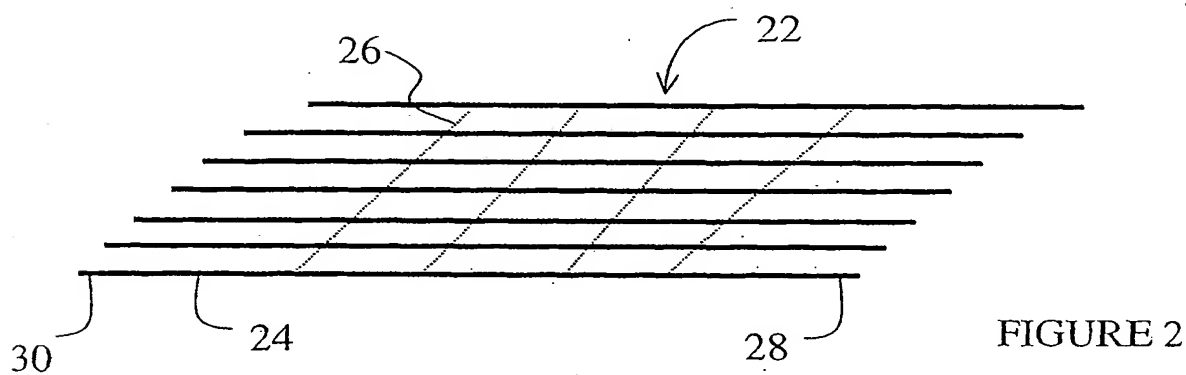
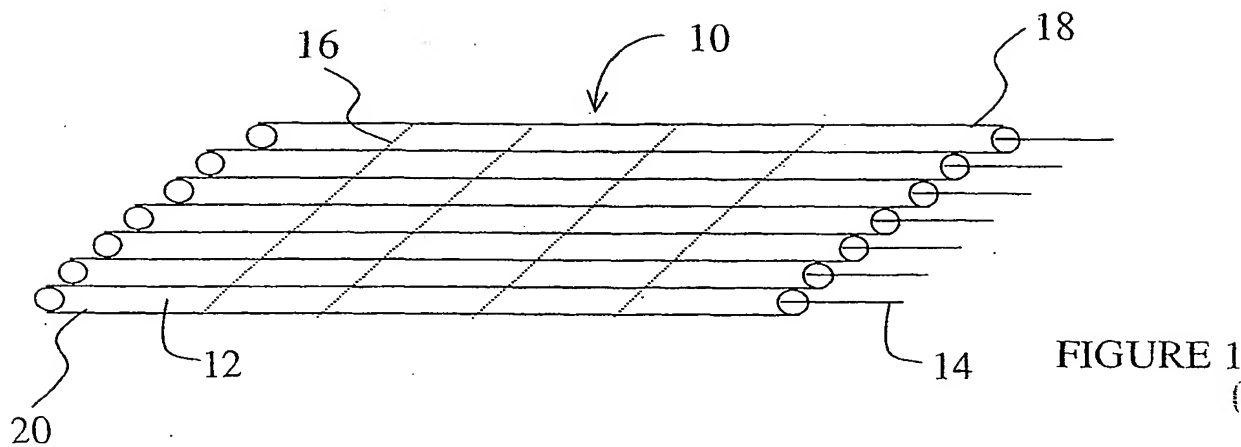
Claims 126-128 have been amended to change the word "tube" into "bore" to more accurately describe the structural characteristics of the applicant's claimed invention.

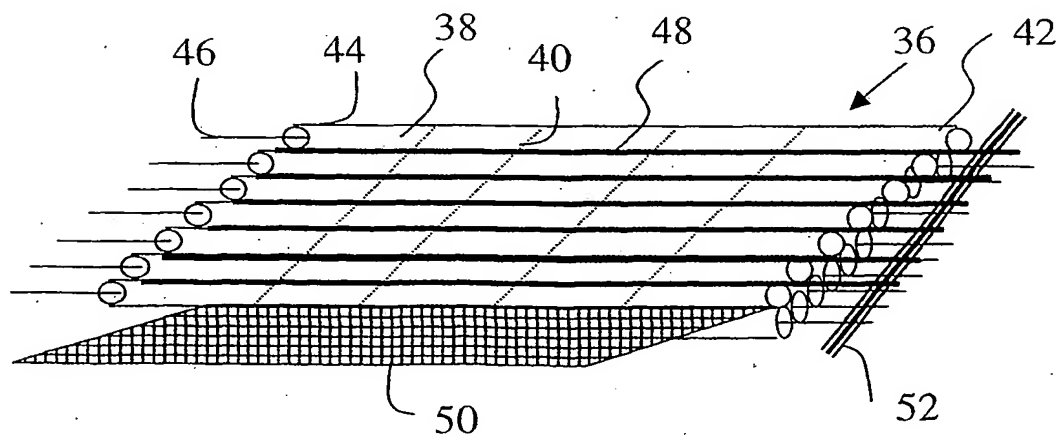
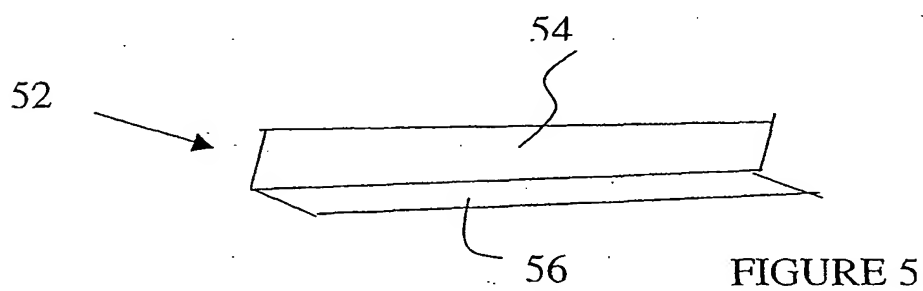
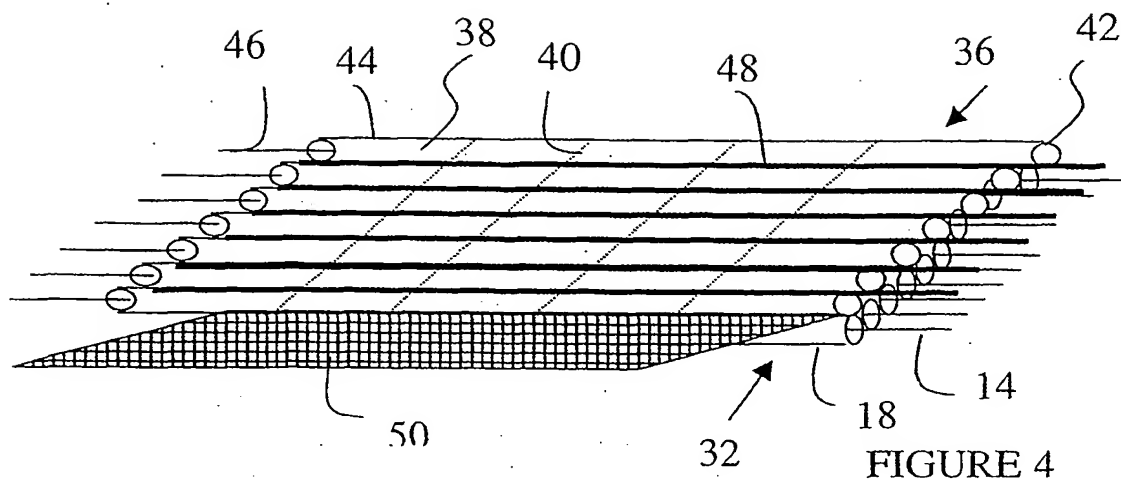
Claims 130, 133, 134, 137, 140, 141, 146, 153-155, 159, and 175 have been amended to recite "hollow, nonporous tubular heat exchange elements".

Claim 214 has been amended to additionally require "a carbon or graphitic current collector in intimate contact with" the coated metal current collector.

Claims 217-219 have been amended to further specify "said current collector" as "said coated metal current collector".

Applicant therefore respectfully requests that international proceedings continue on the basis of the claims 1-8, 10-34, 36-182, 189-195, and 202-247 present in the application upon entry of the new enclosed pages 59-111.









4/27

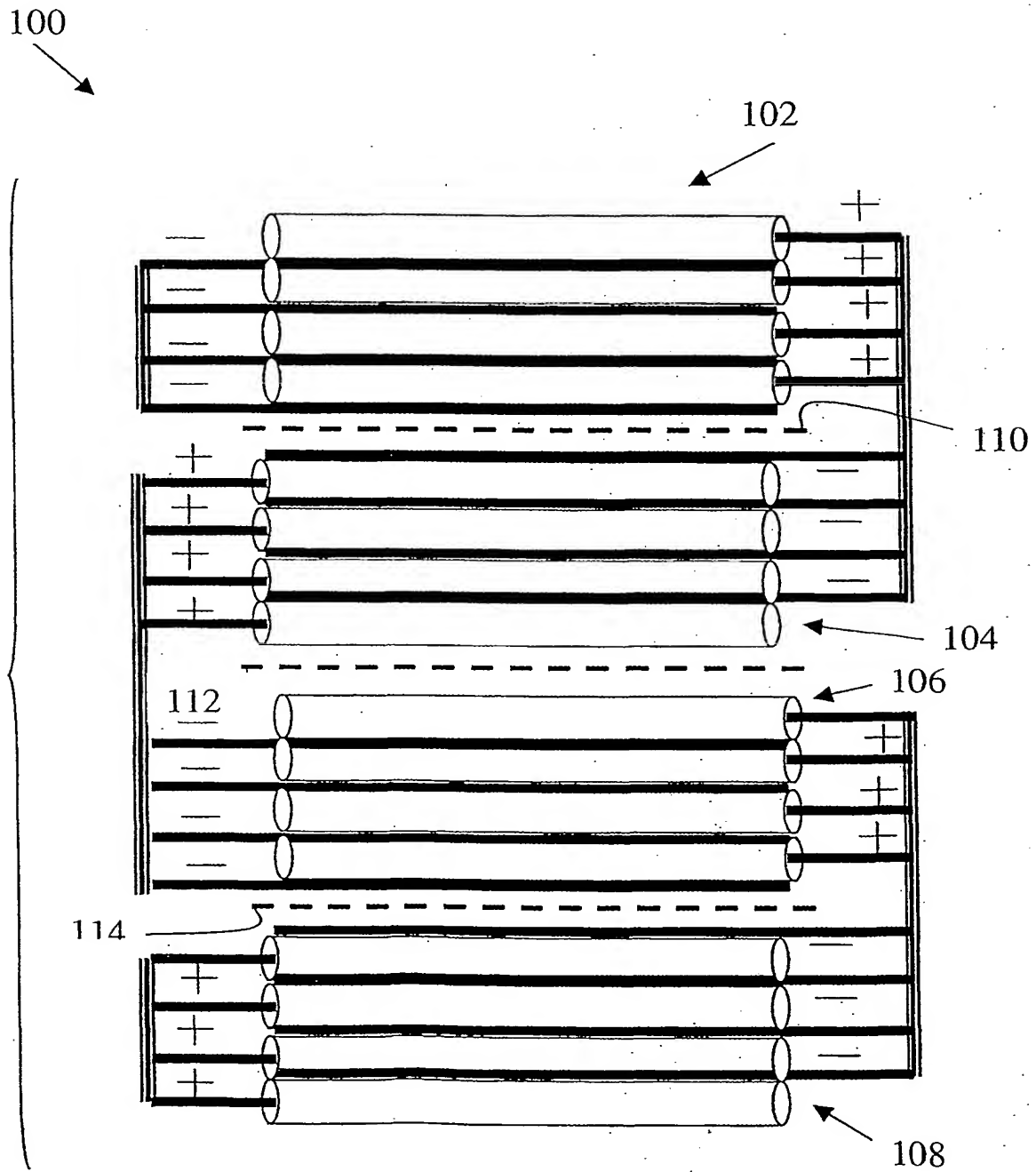
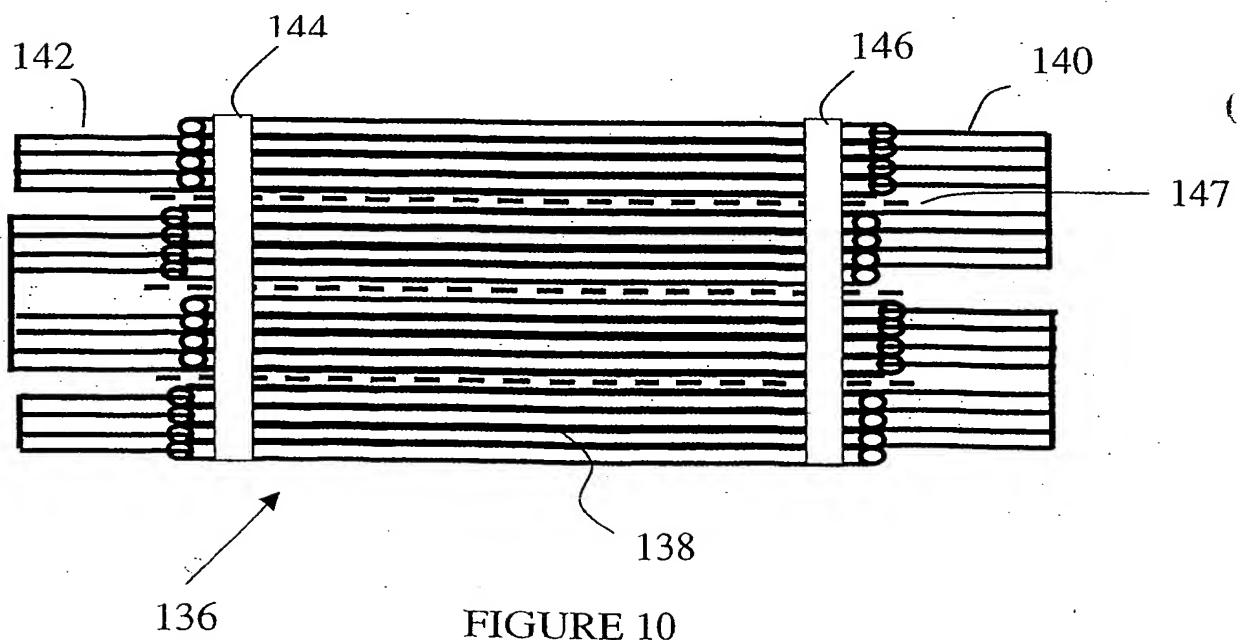
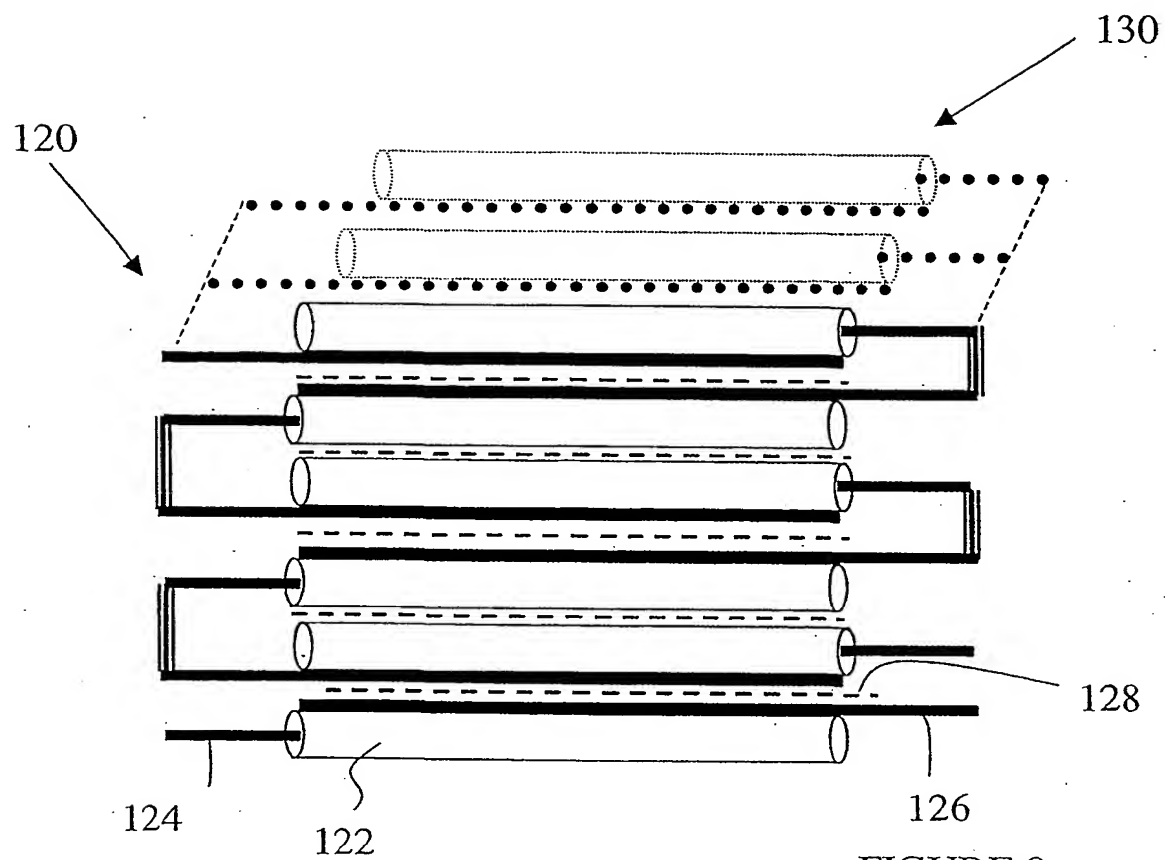


FIGURE 8

5/27



6/27

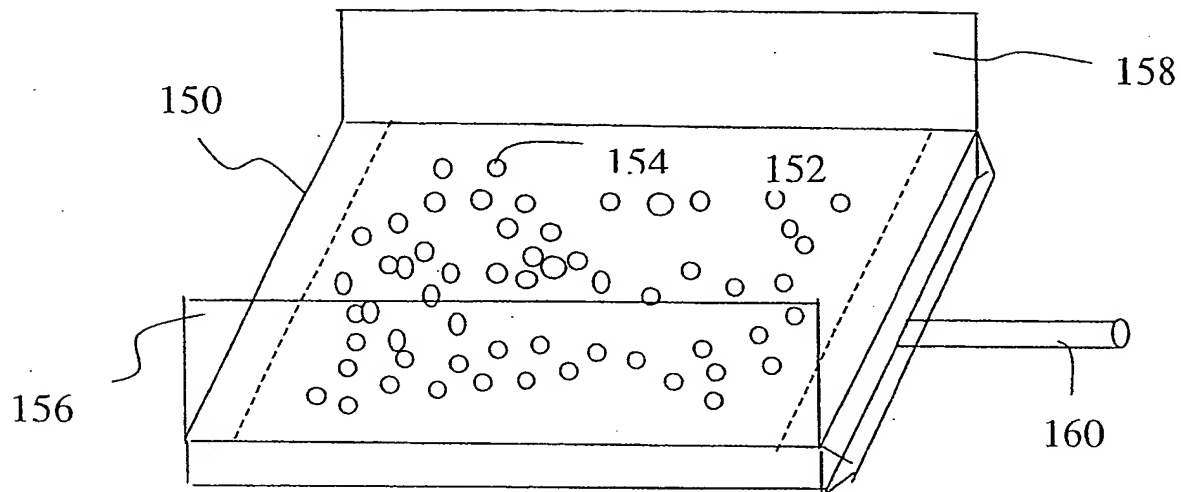


FIGURE 11

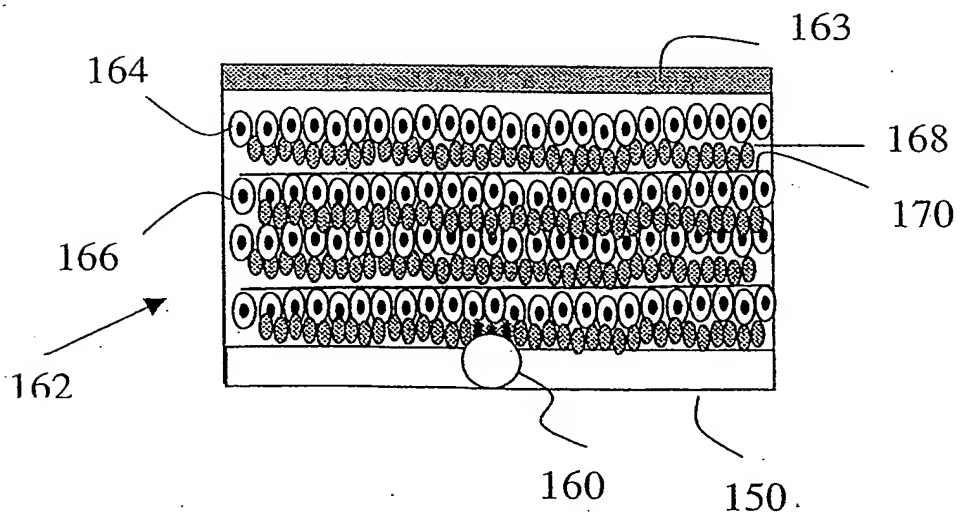


FIGURE 12

7/27

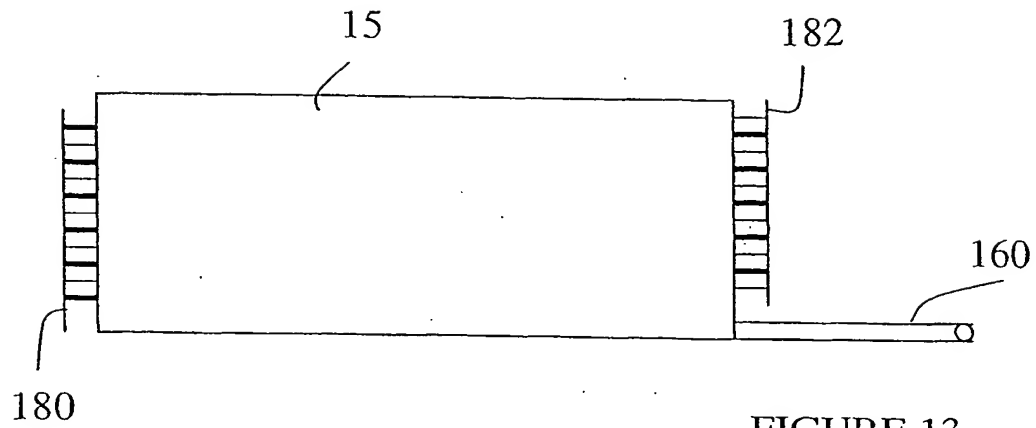


FIGURE 13

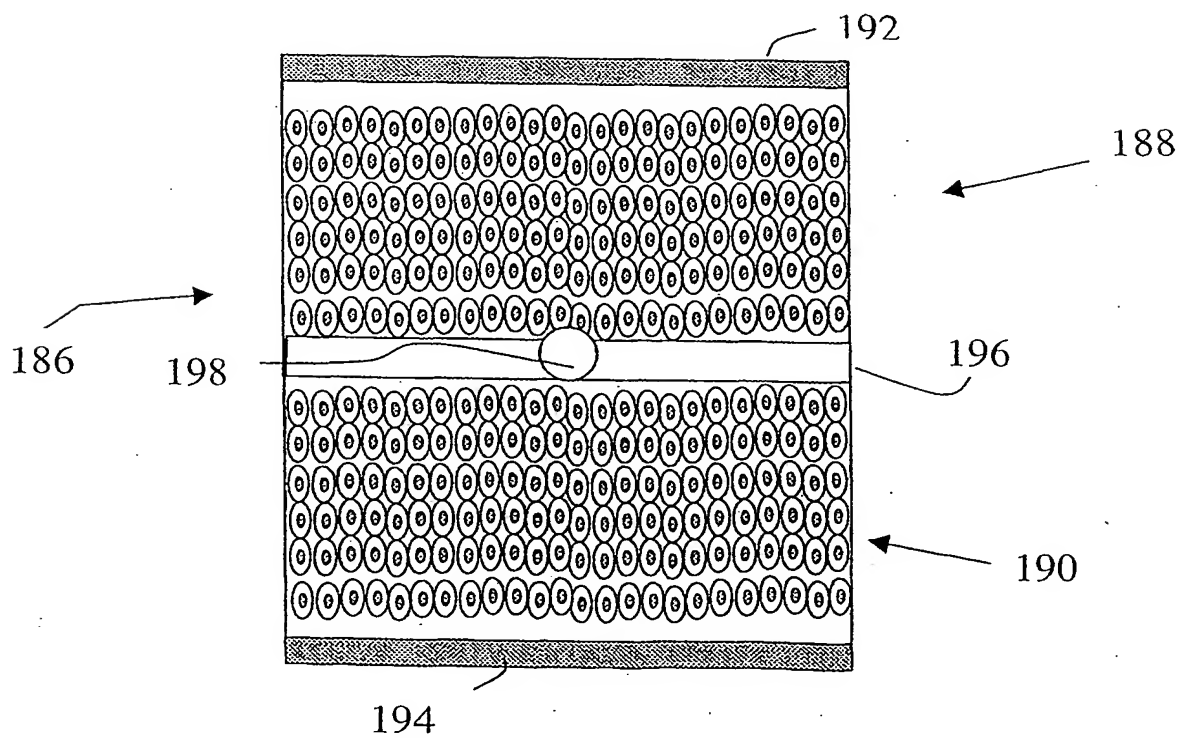


FIGURE 14

8/27

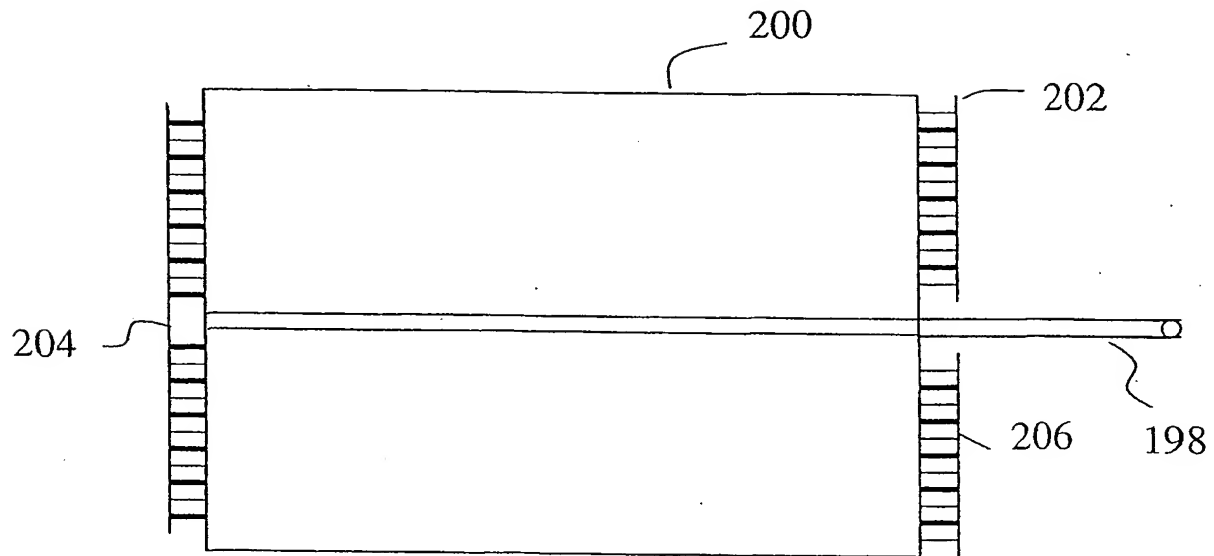


FIGURE 15

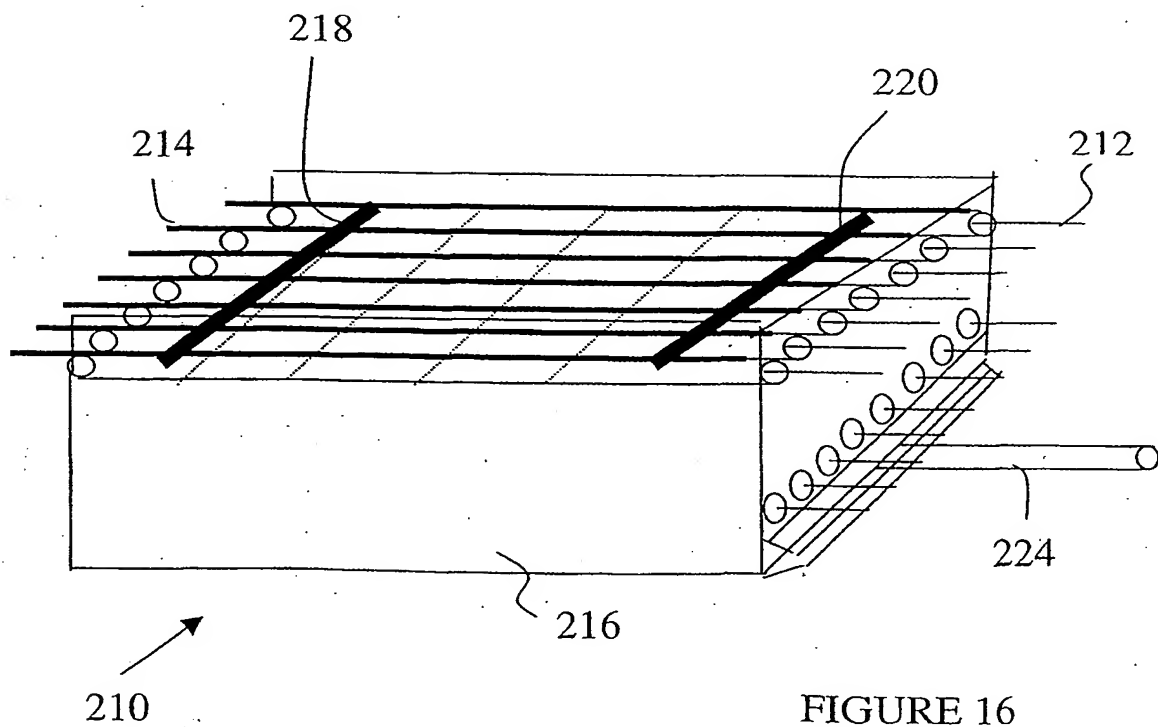


FIGURE 16

9/27

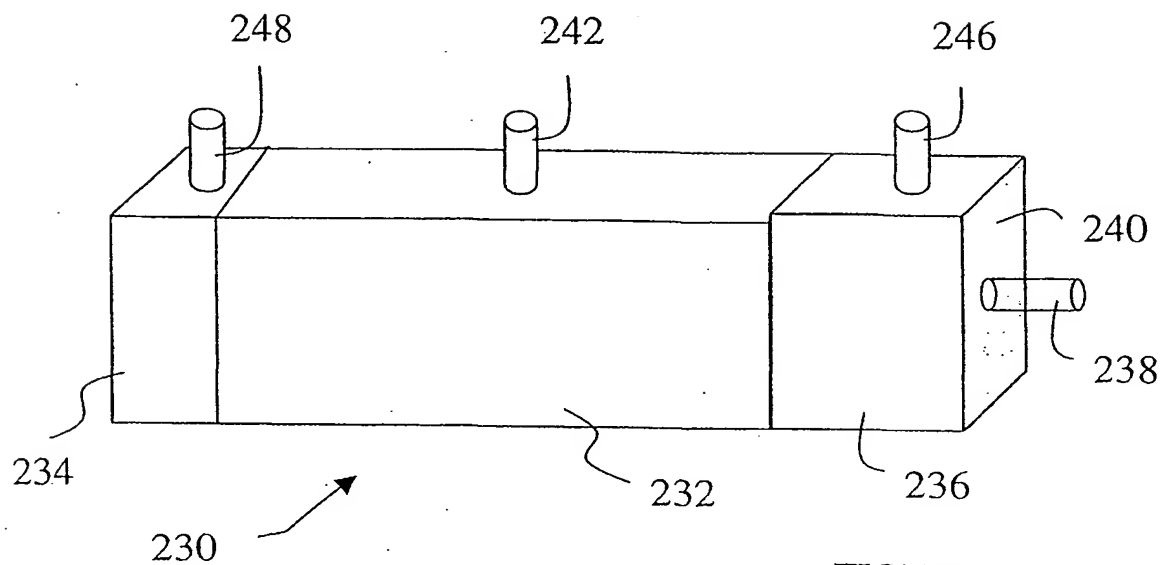


FIGURE 17

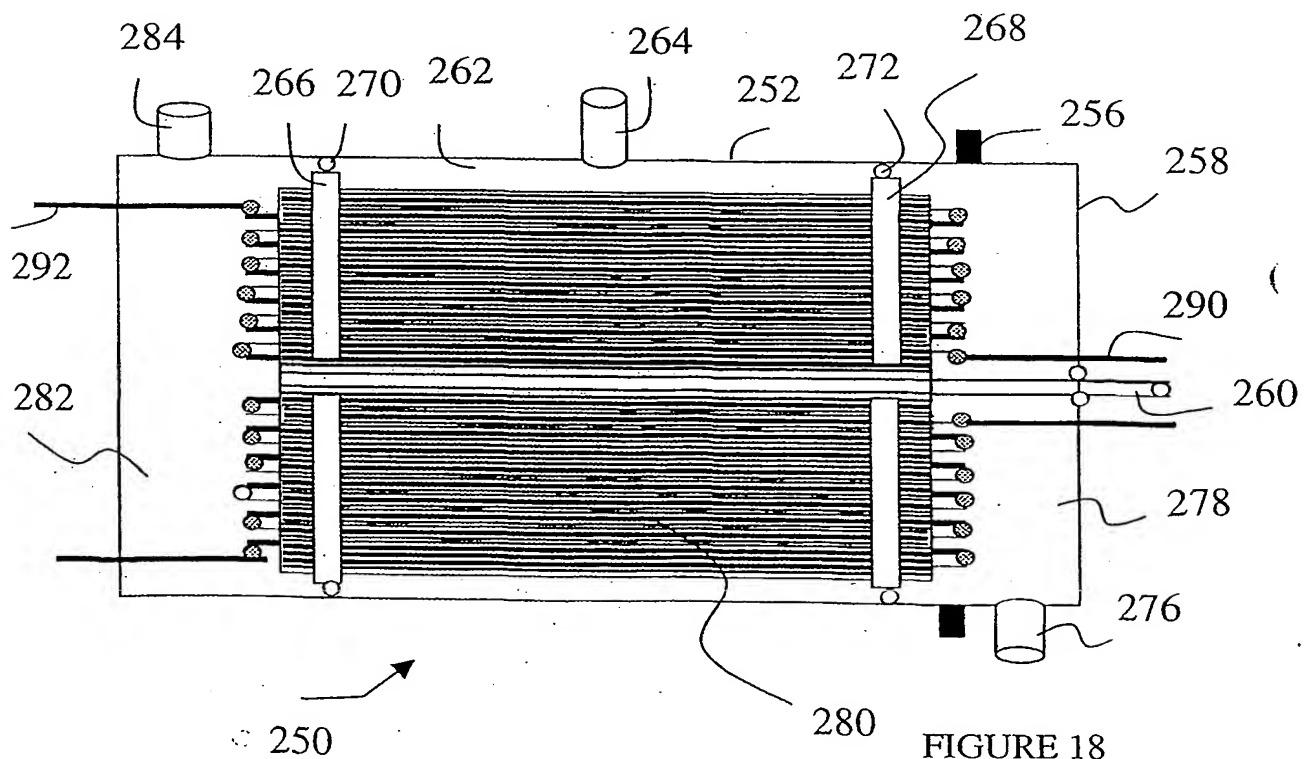


FIGURE 18

10/27

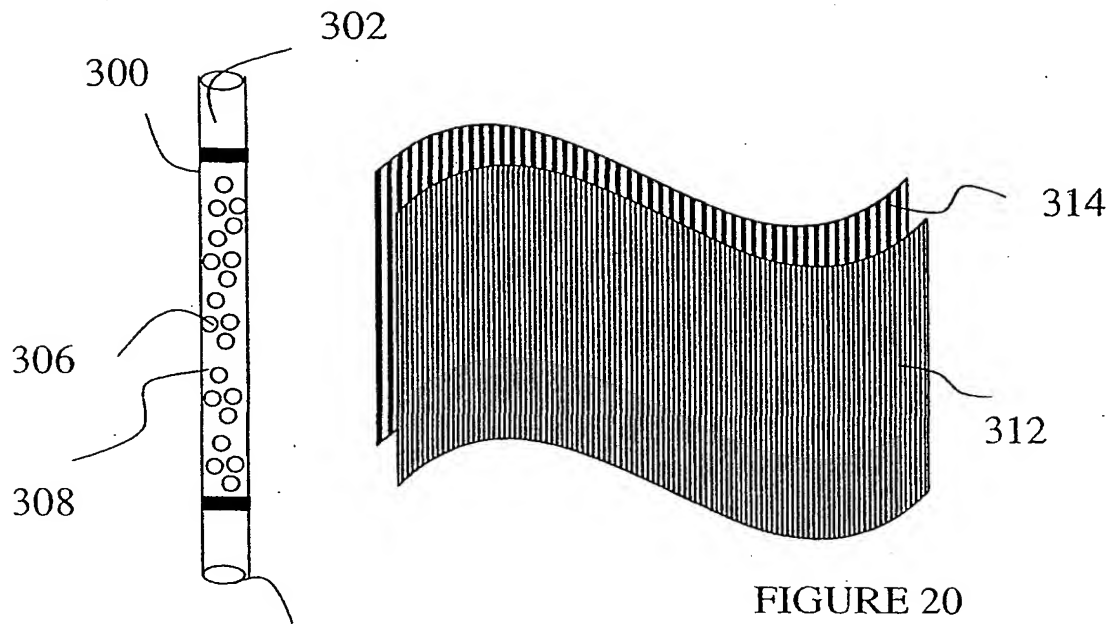


FIGURE 20

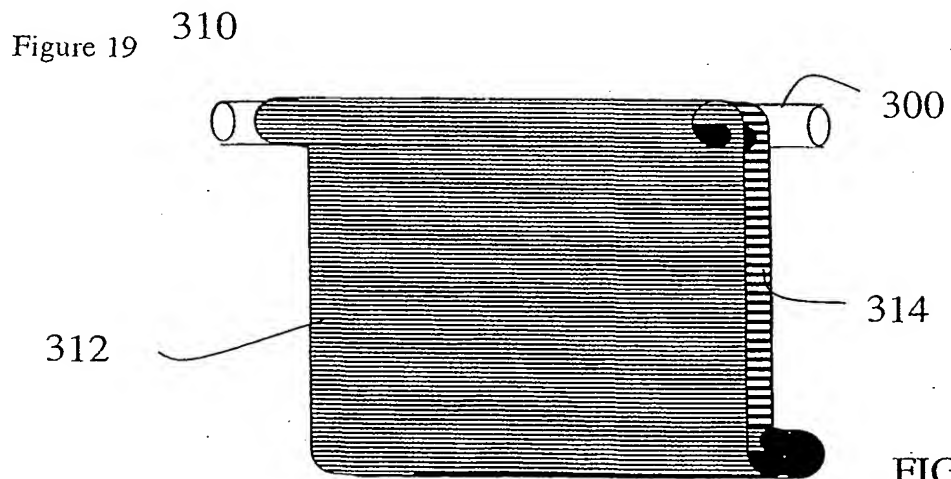


FIGURE 21

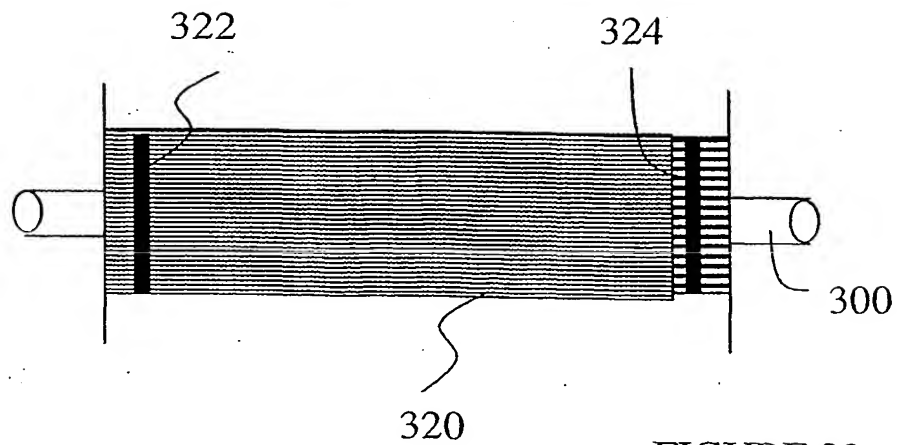


FIGURE 22

11/27

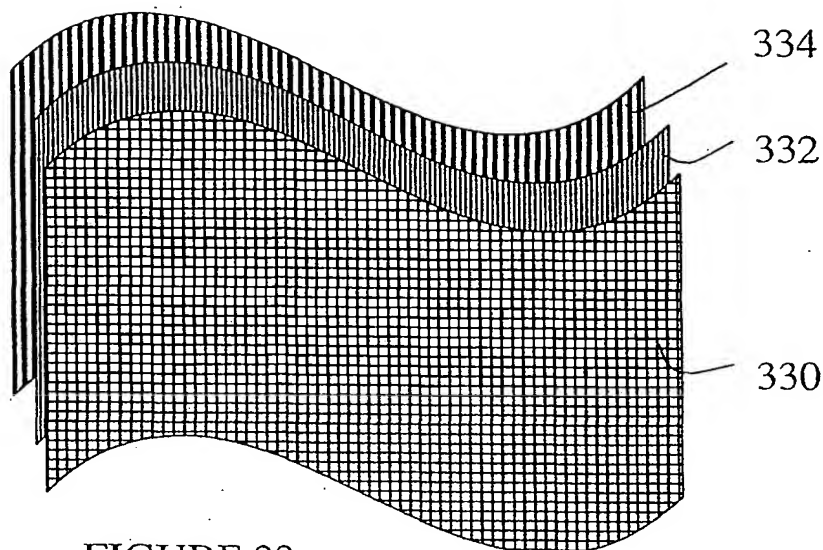


FIGURE 23

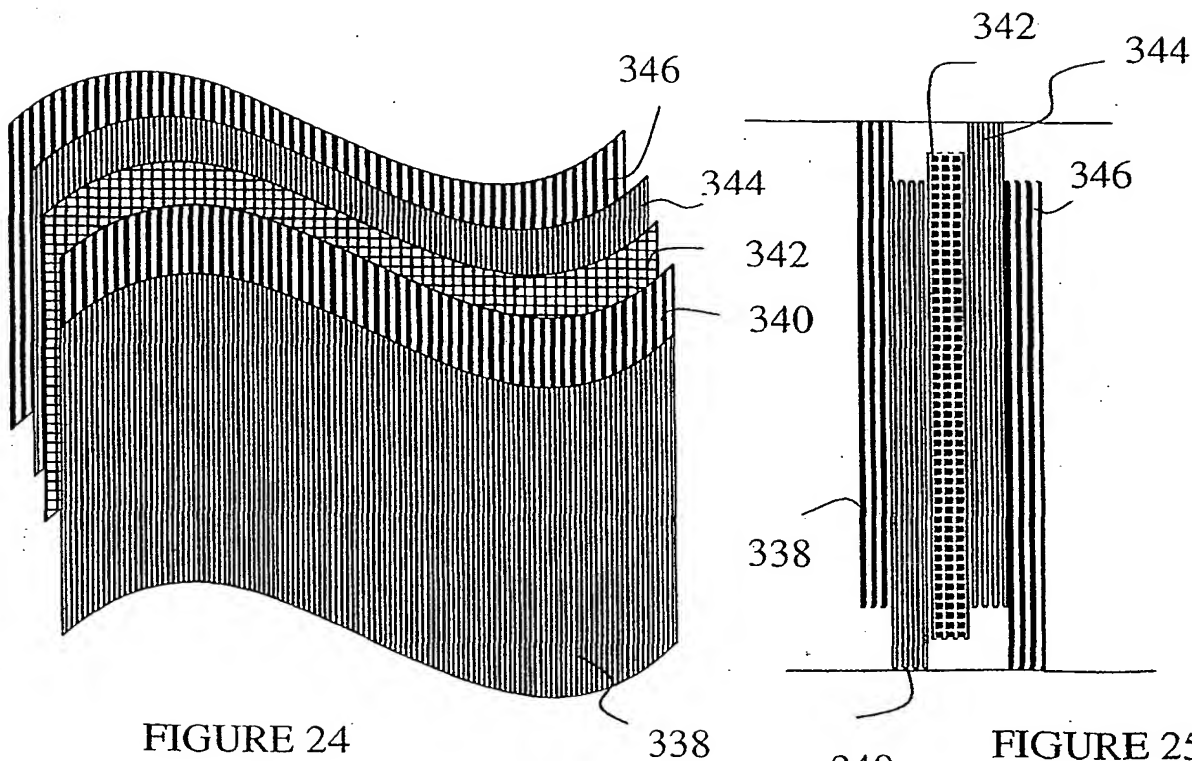


FIGURE 24

FIGURE 25



12/27

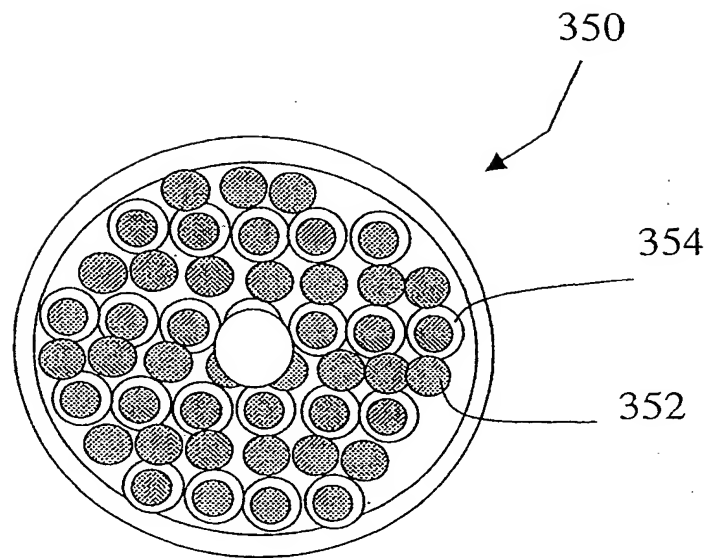


FIGURE 26

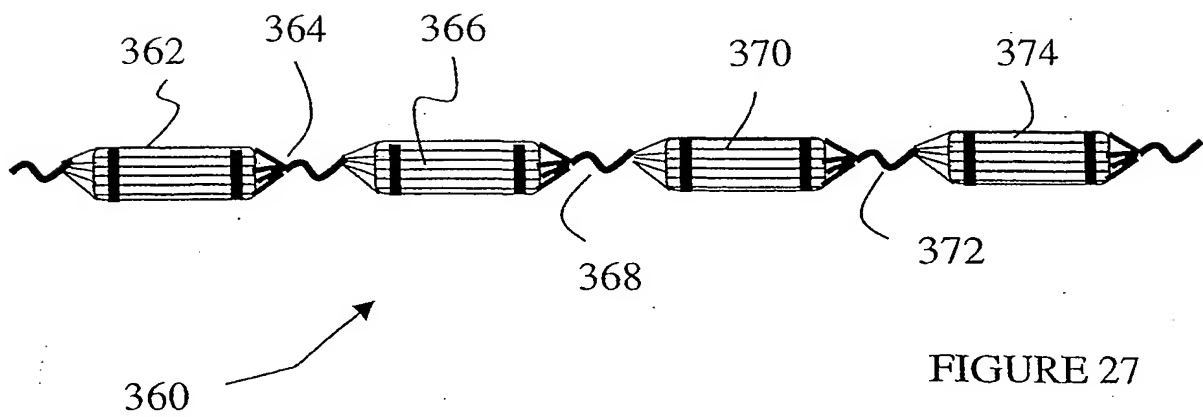


FIGURE 27

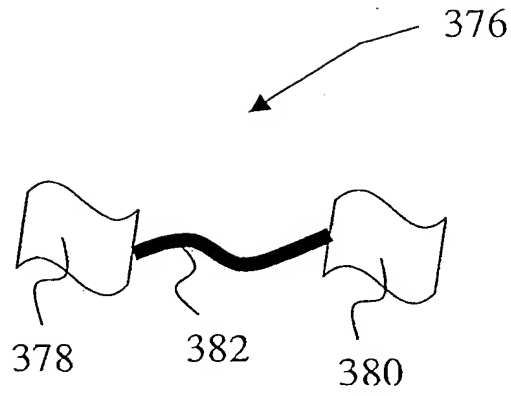


FIGURE 28

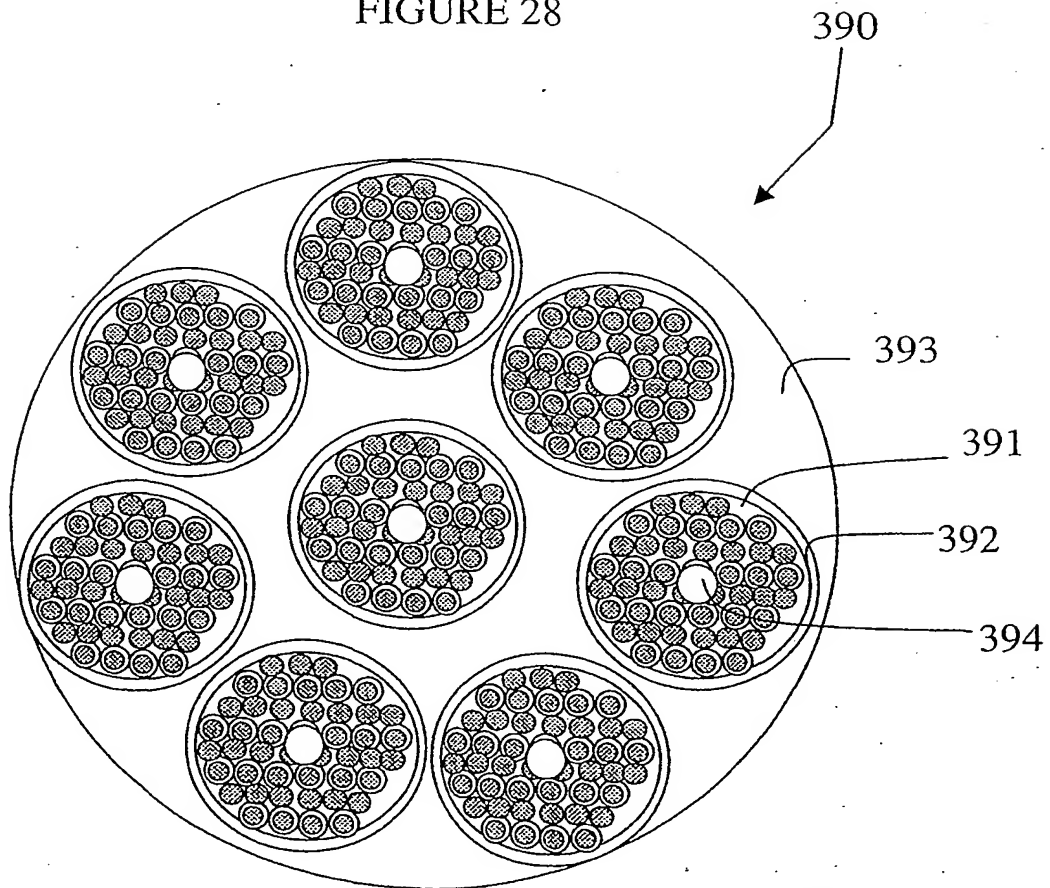
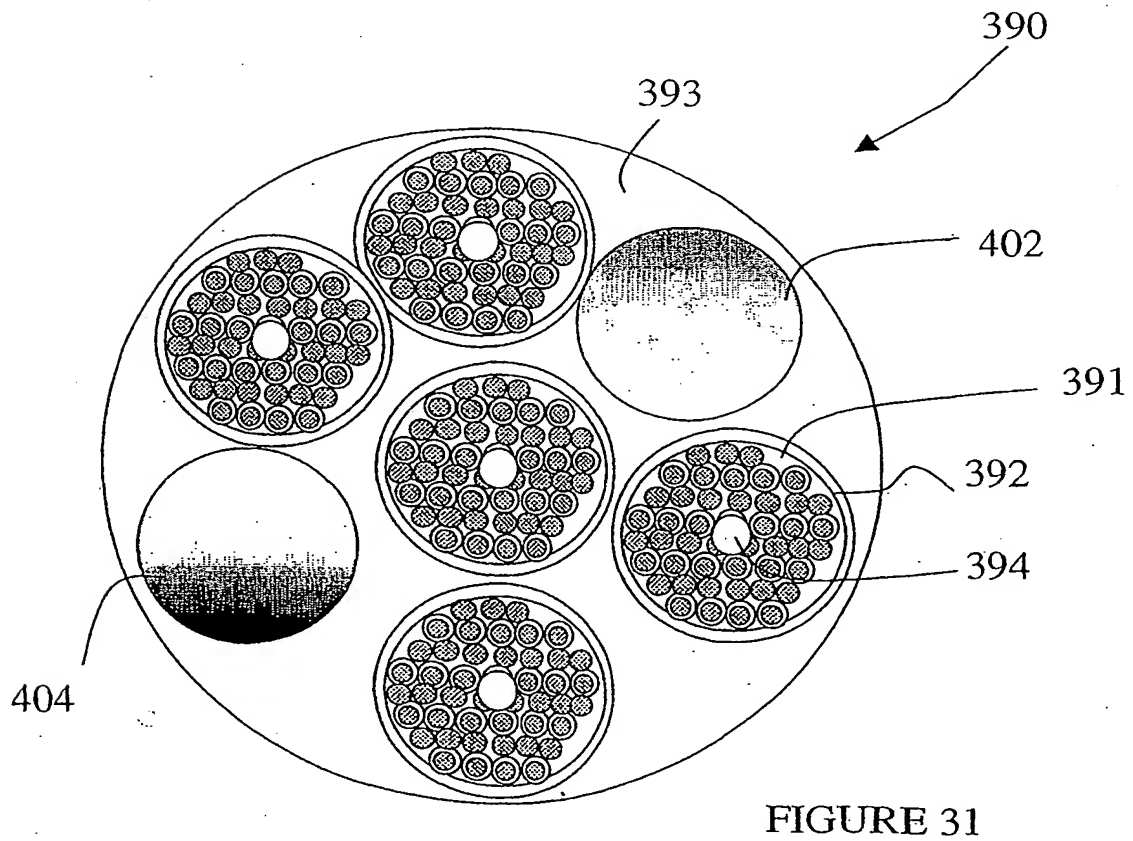
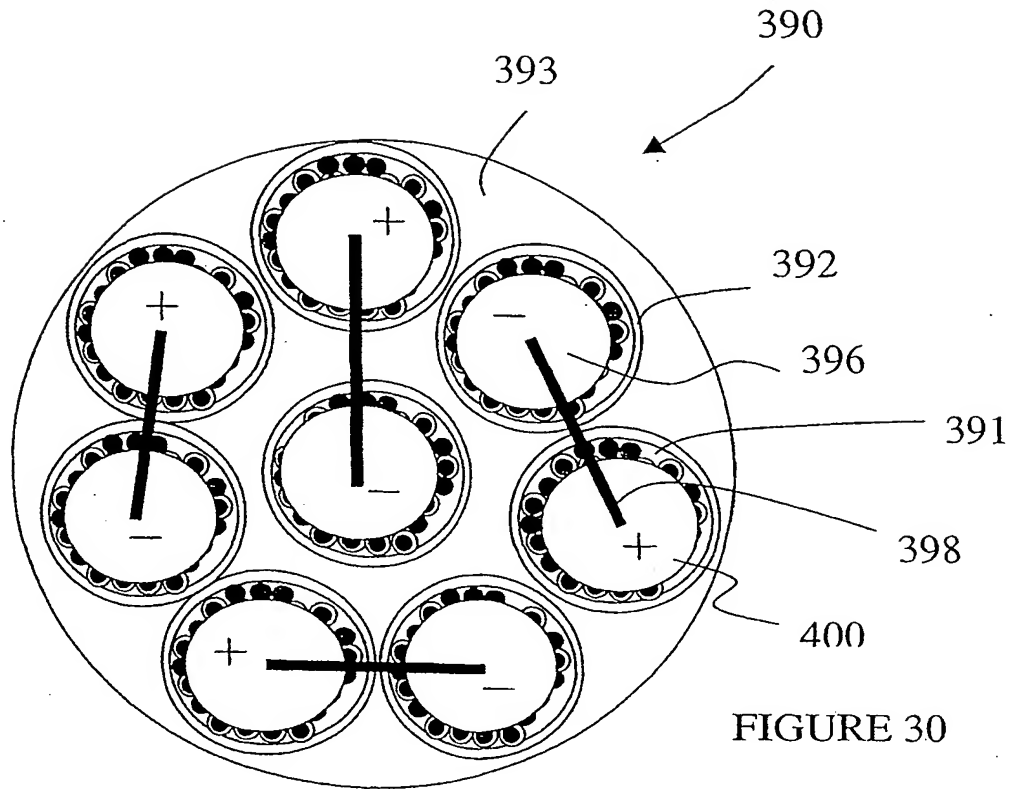
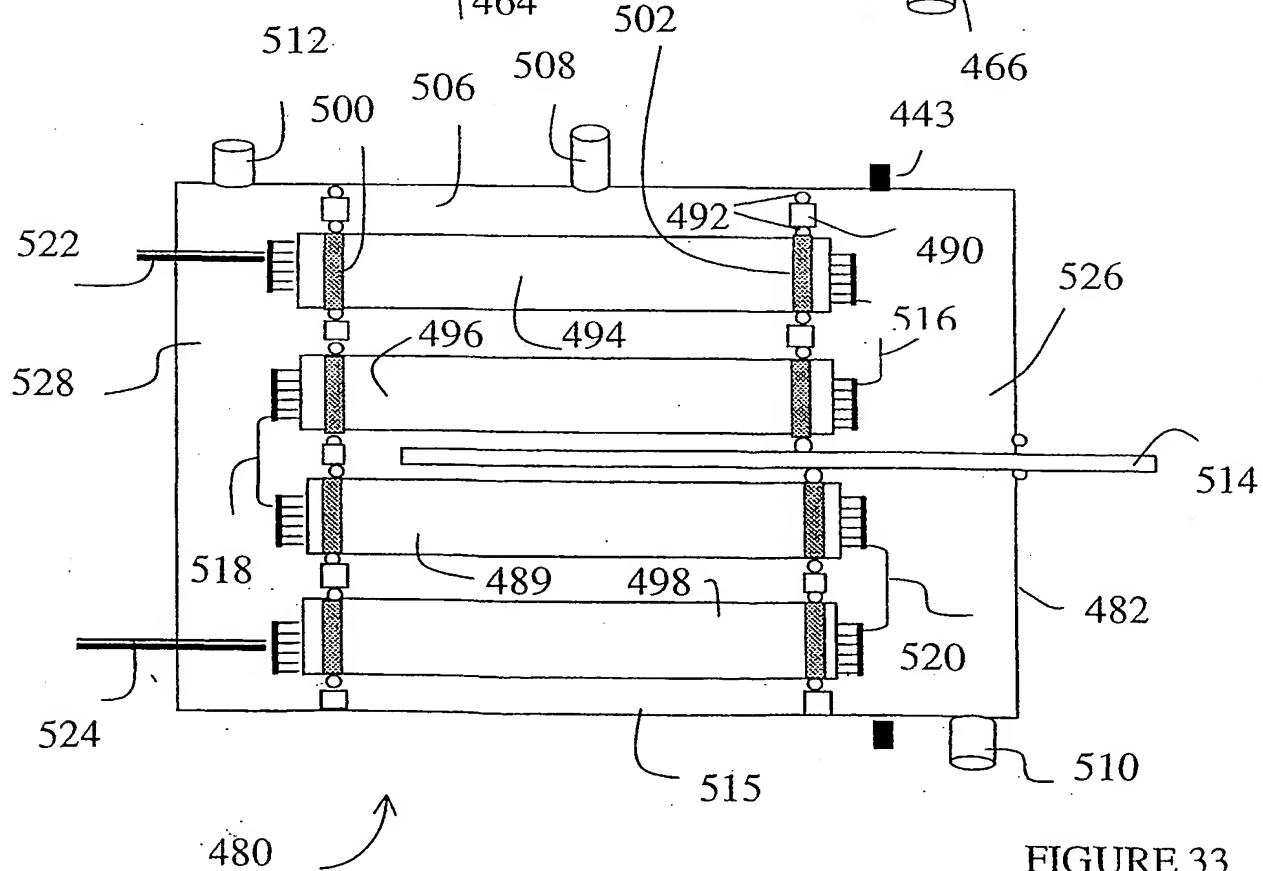
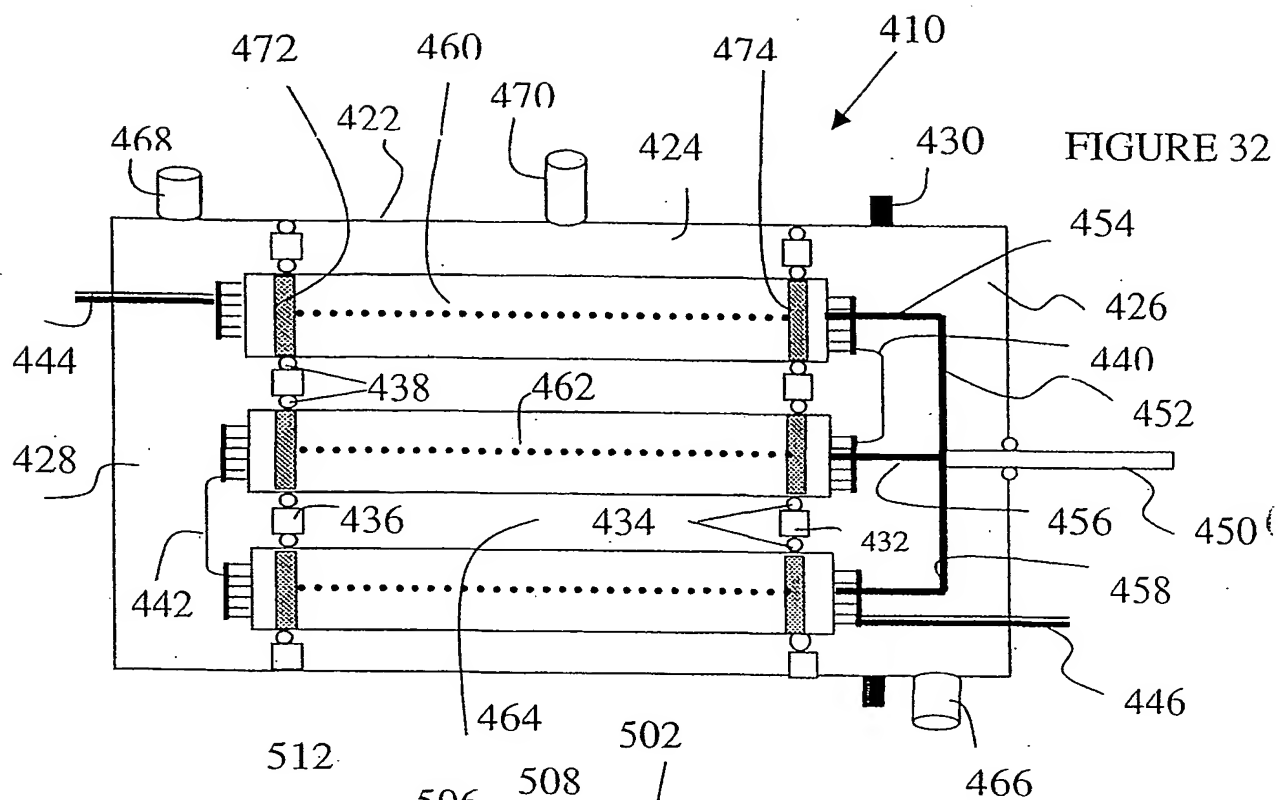


FIGURE 29

14/27





16/27

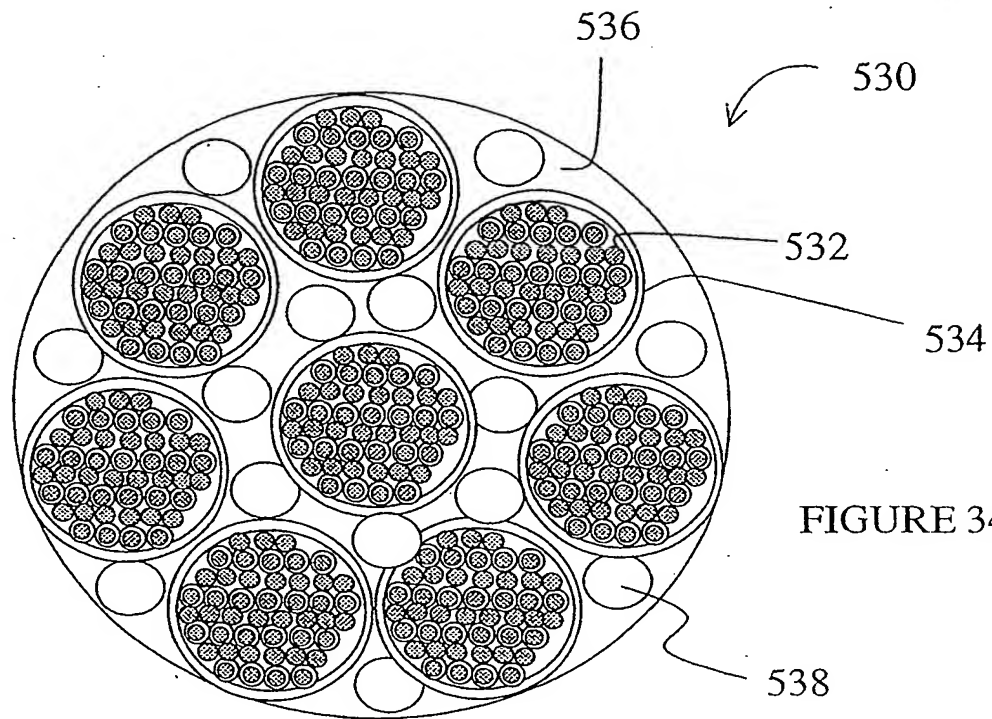


FIGURE 34

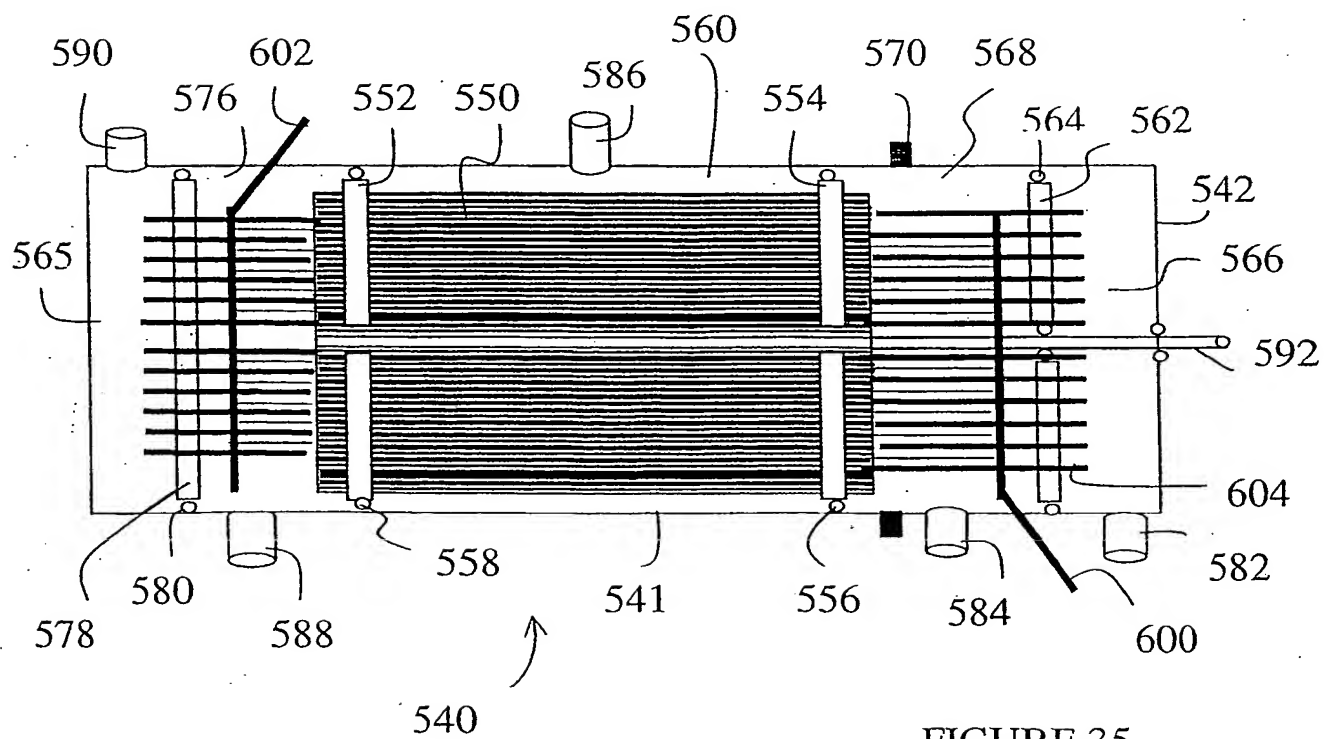
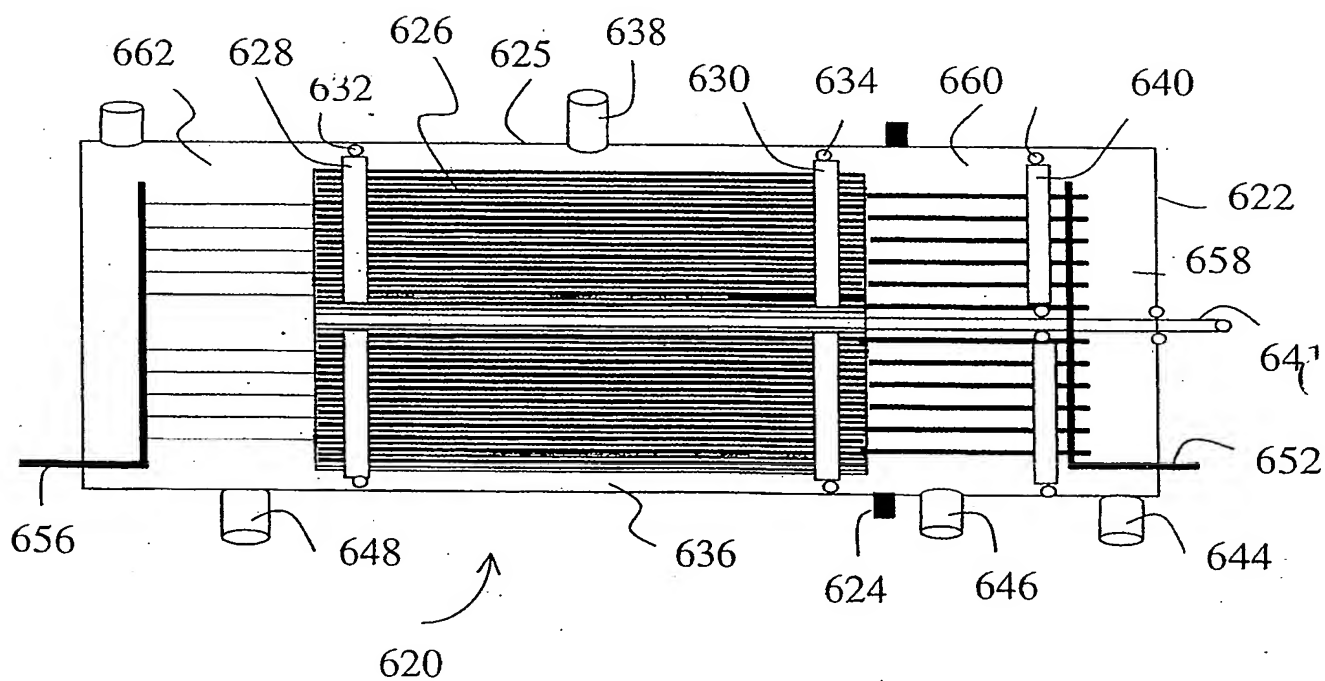
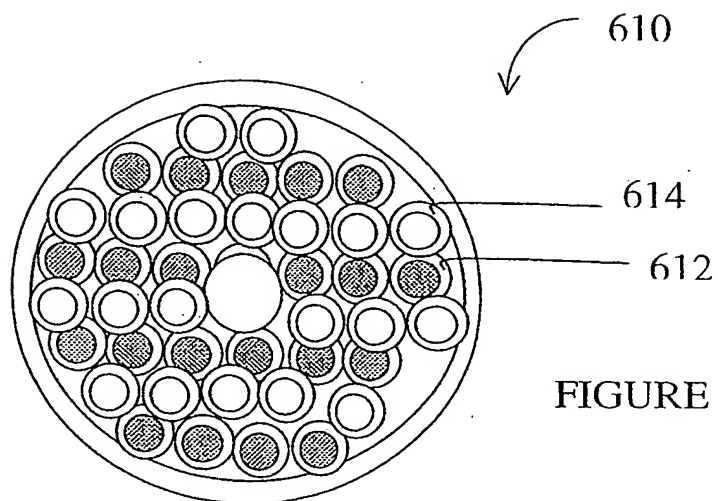


FIGURE 35



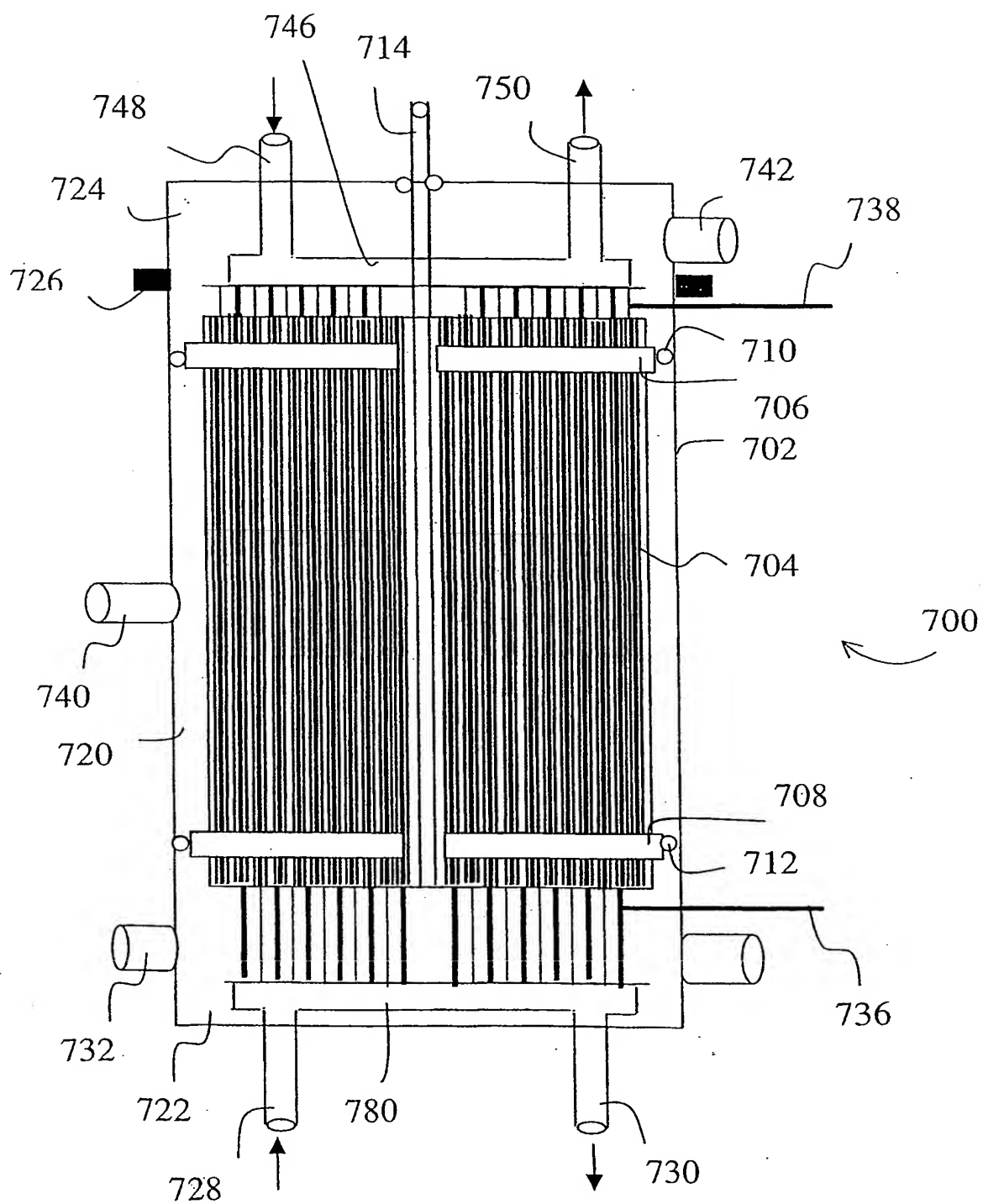


FIGURE 38

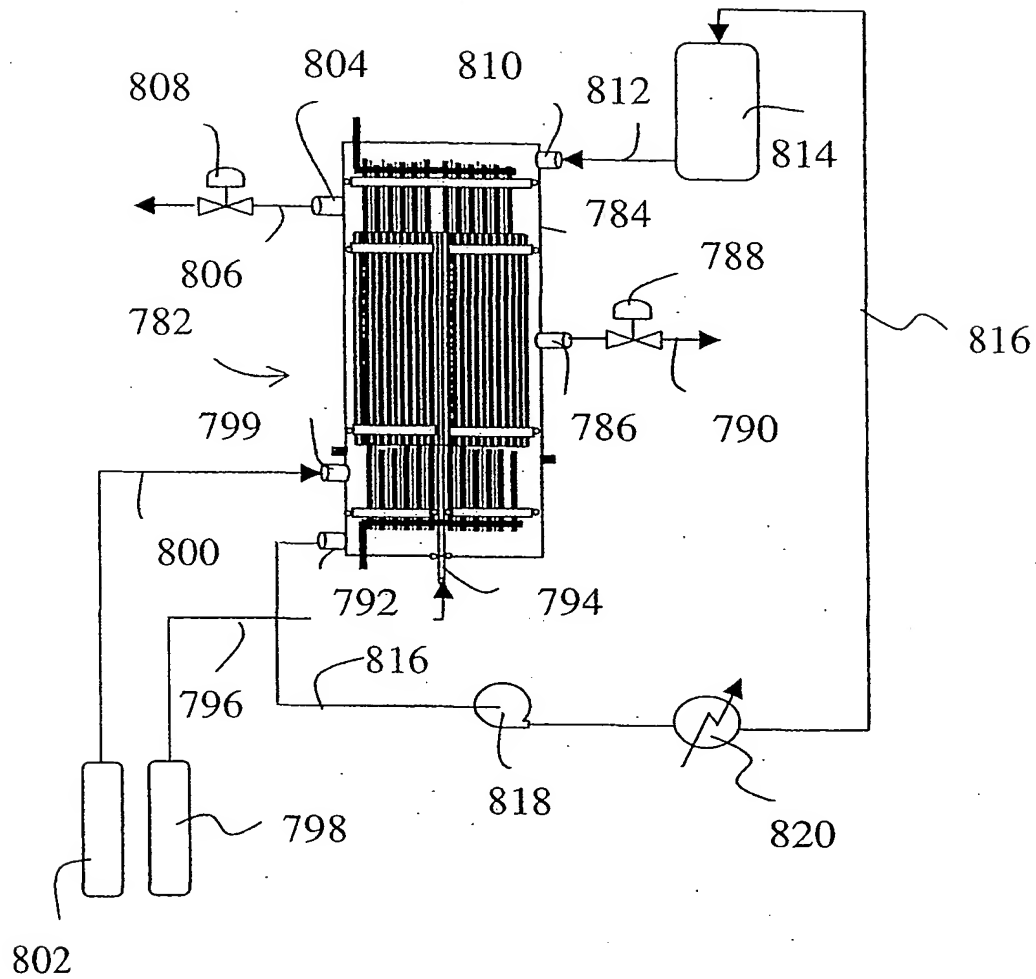
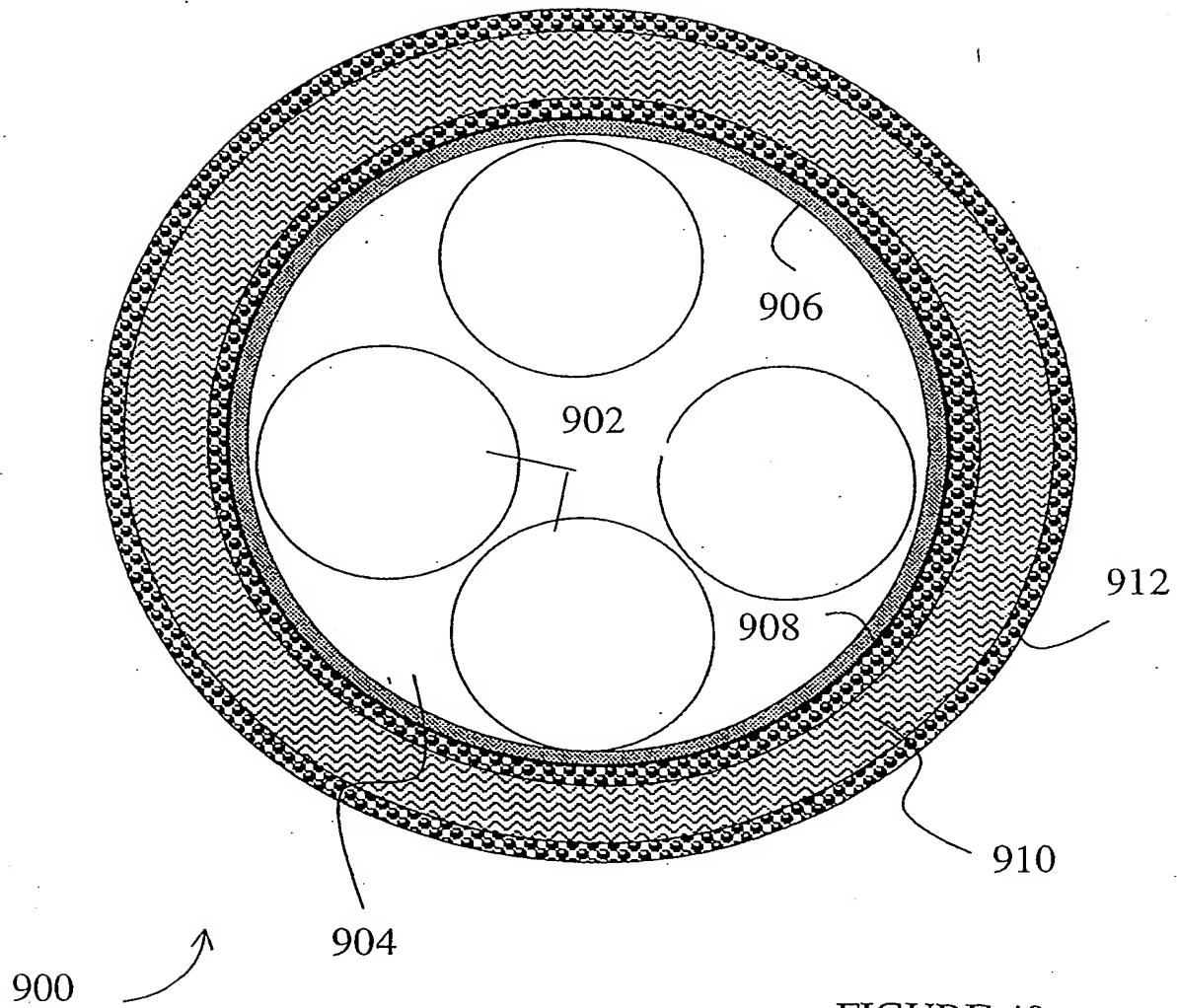


FIGURE 39





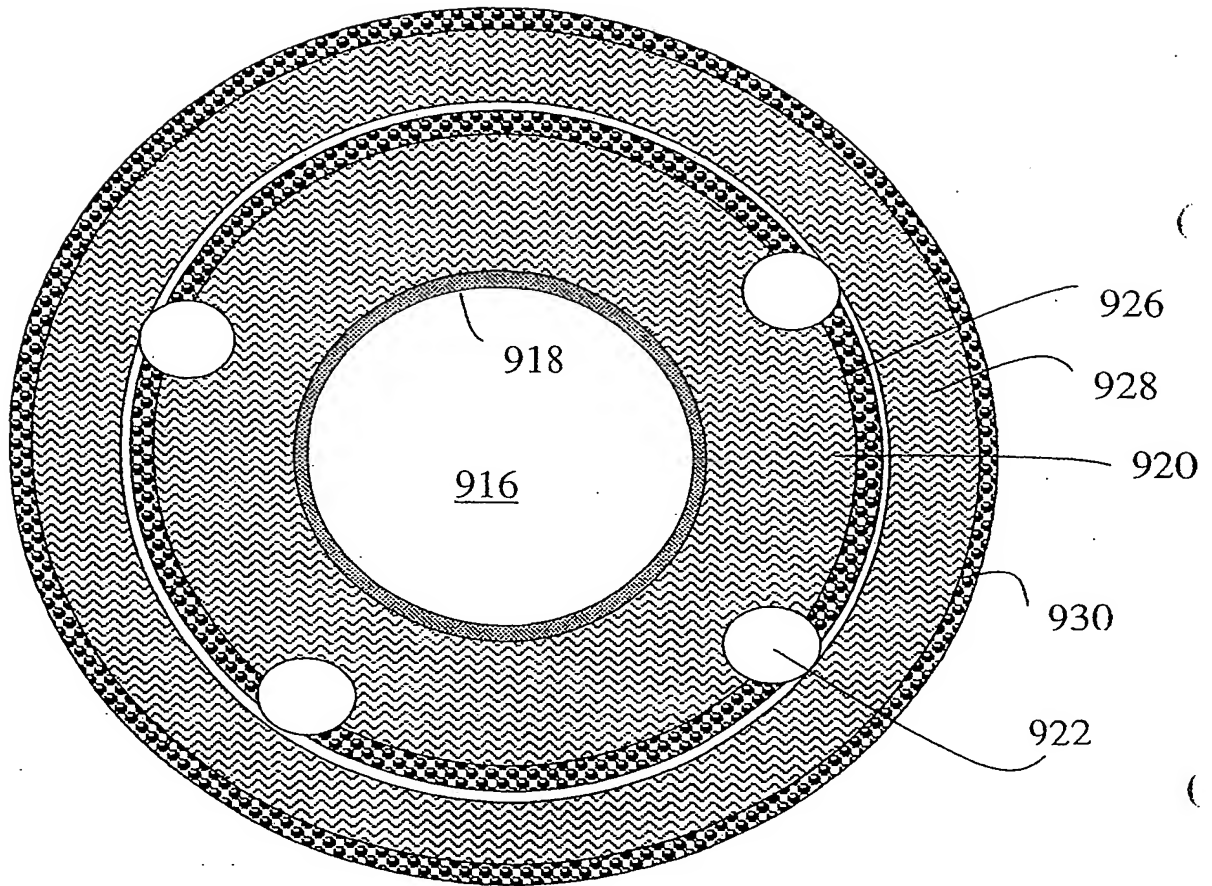


FIGURE 41

914

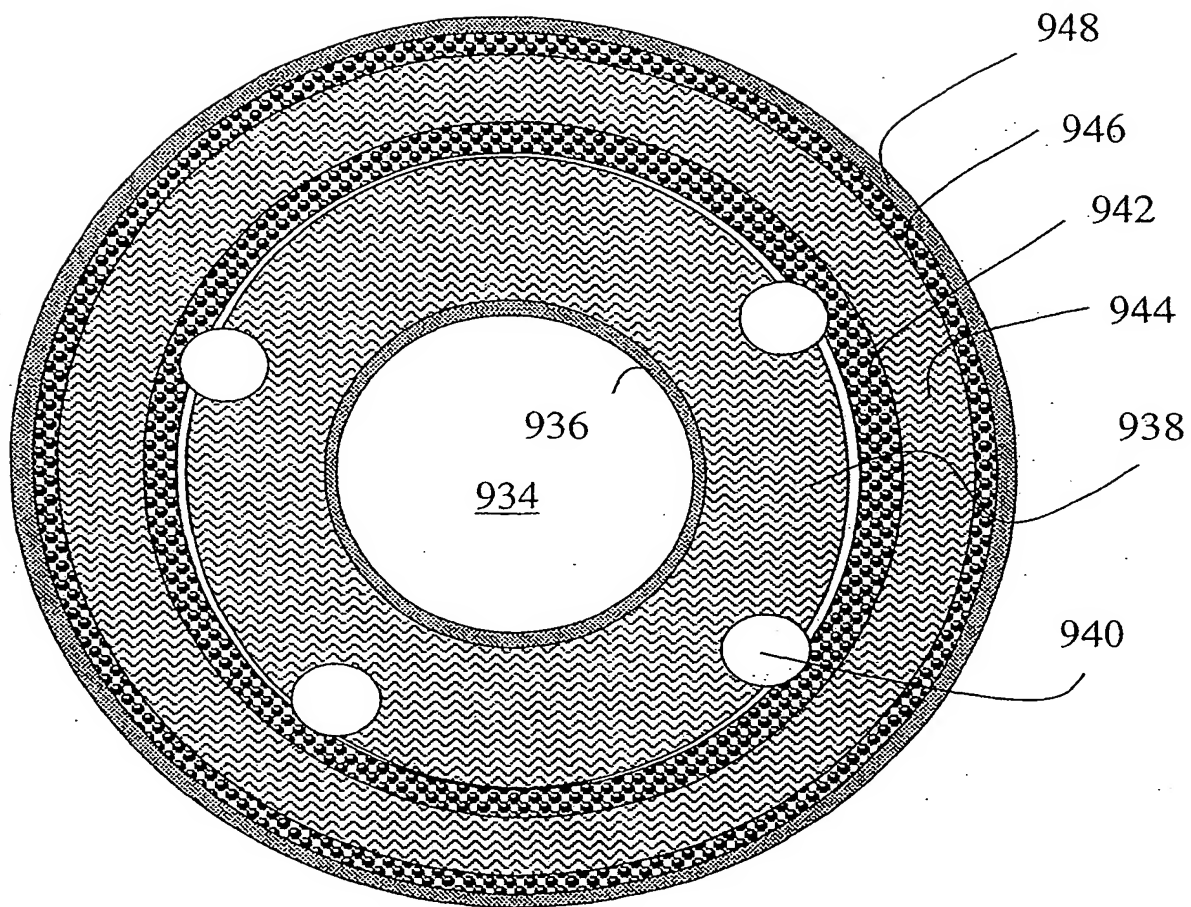


FIGURE 42

932

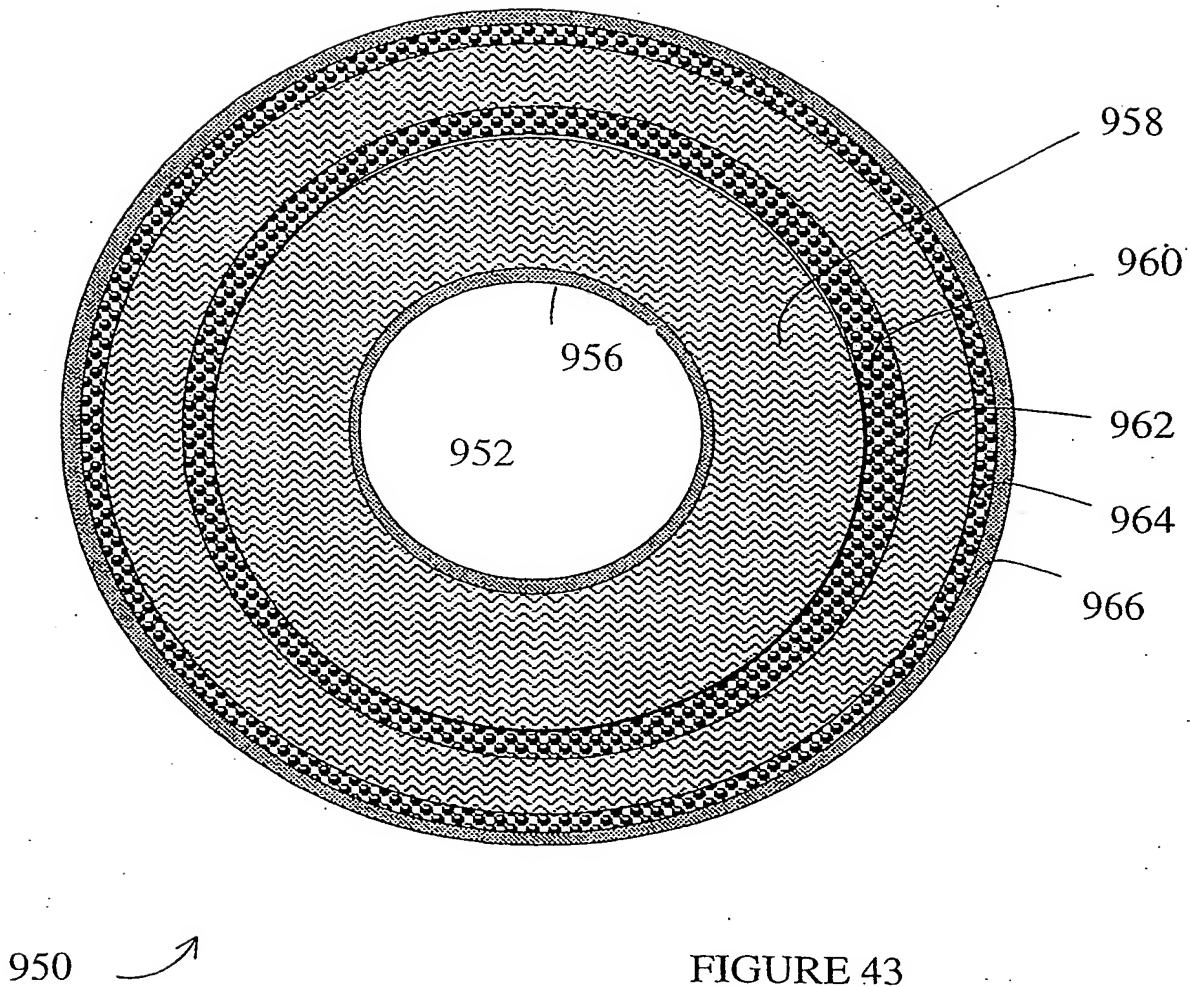


FIGURE 43

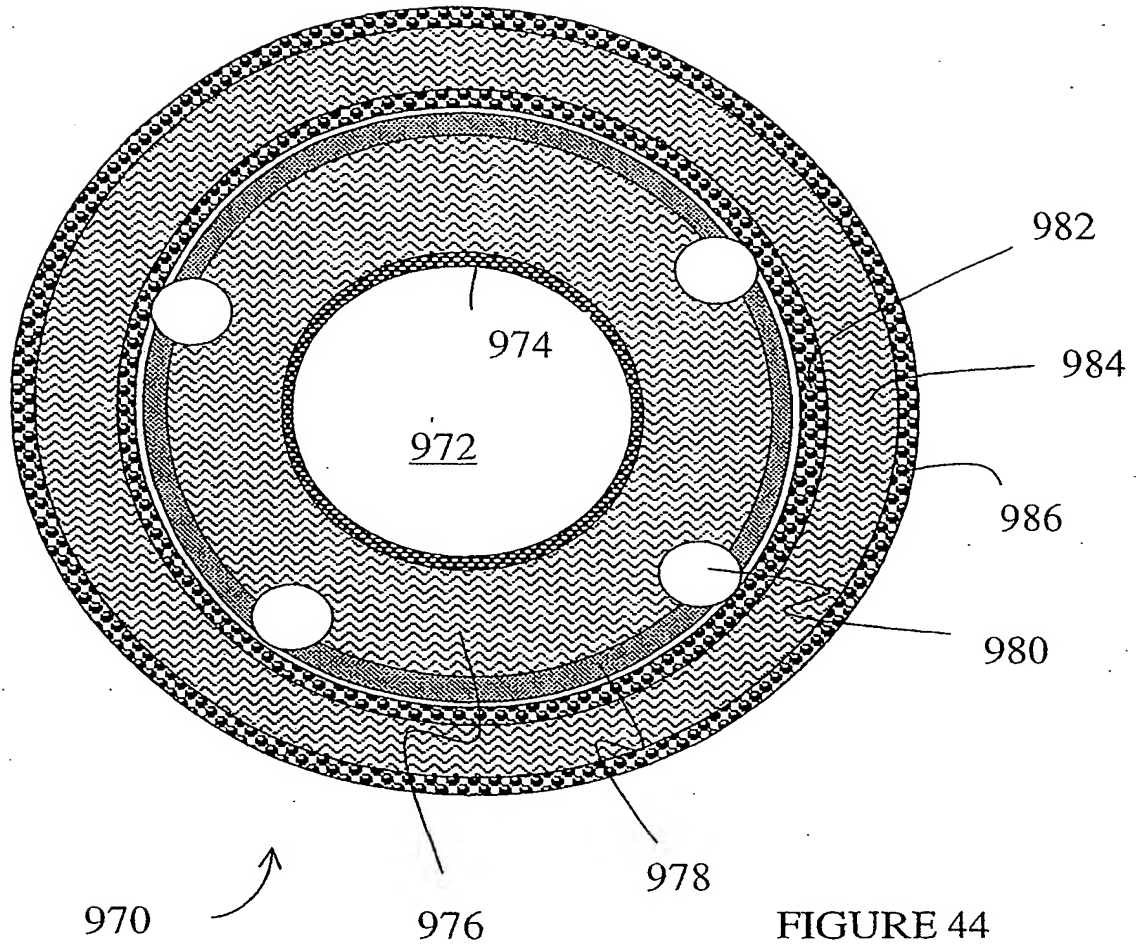


FIGURE 44

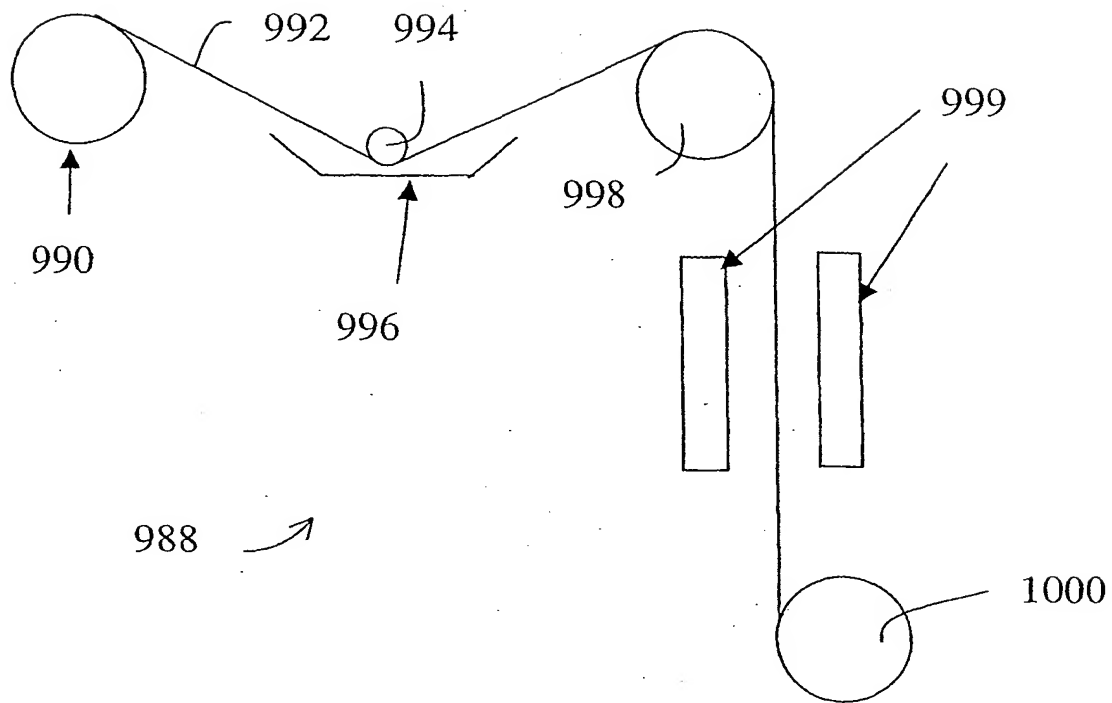


FIGURE 45

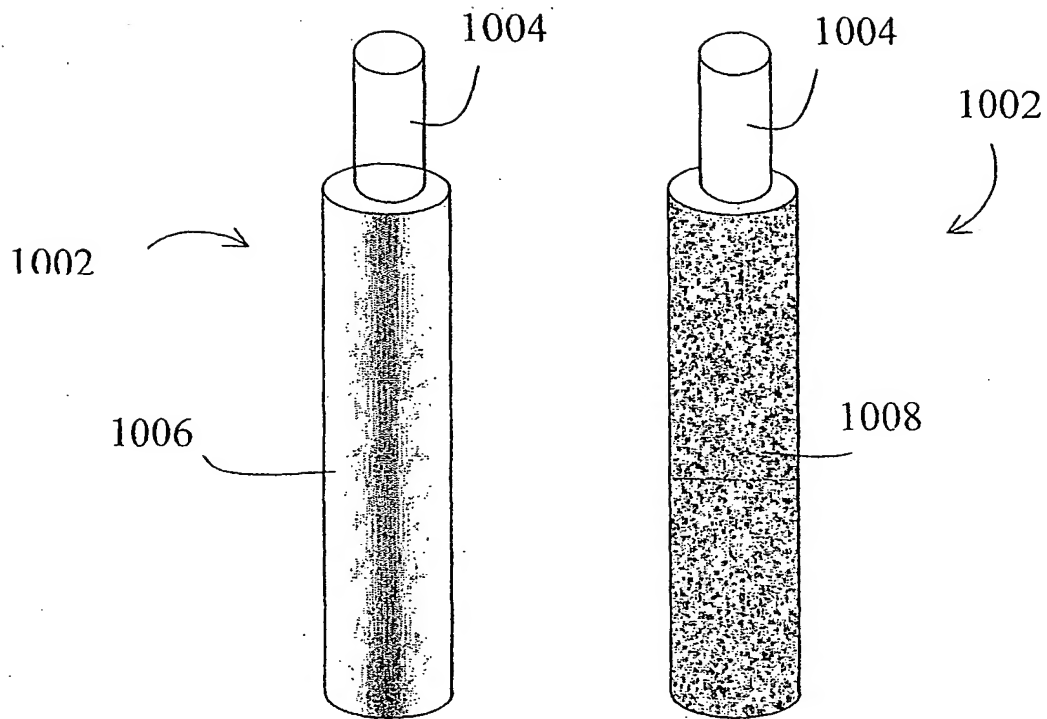


FIGURE 46

FIGURE 47

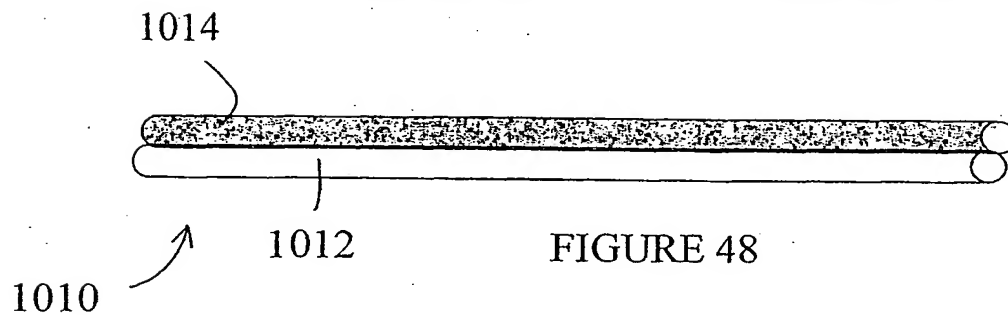


FIGURE 48

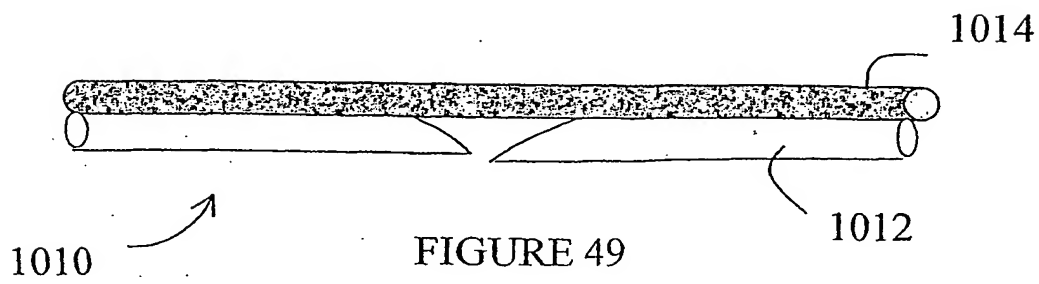
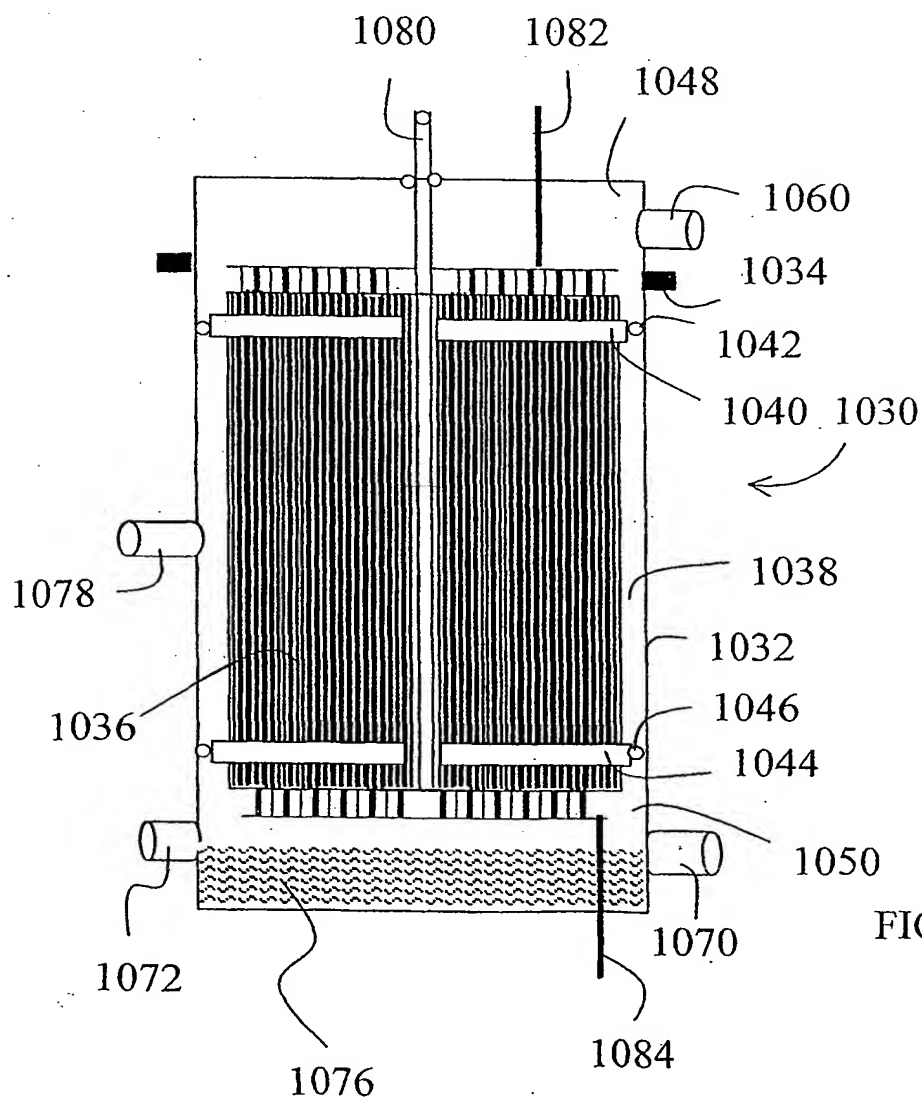
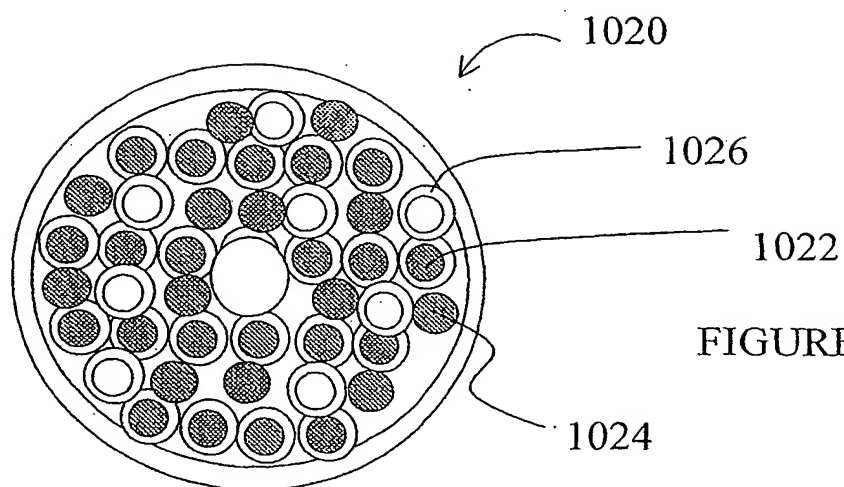


FIGURE 49

27/27





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/23220

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : H01M 02/18, 04/86, 04/88, 06/10, 06/44

US CL : 429/40-45, 94, 127, 131-133, 211; 29/623.1-623.5; 502/101

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/27, 40-45, 94, 127, 131-133, 136, 137, 140, 141, 164, 209, 211; 29/623.1-623.5; 502/101

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Please See Continuation Sheet**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 09-223507 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 26 August 1997 (26.08.1997), see abstract, Figures 1-3, paragraph 8, lines 14-17 and paragraph 39.	183, 196
---		
Y		130-182, 184-195, 197-201
X	US 4,123,596 A (ROBINSON) 31 October 1978 (31.10.1978), column 2, lines 25-32 and lines 60-61; column 3, lines 38-41; column 4, lines 12-14 and lines 45-49.	202-204, 207, 209
X	US 5,916,514 A (ESHRAHGI) 29 June 1999 (29.06.1999), column 2, lines 34-44; column 3, lines 51-55; column 5, lines 1-47; column 6, lines 1-20; column 7, lines 10-42; column 8, lines 65-67; column 9, lines 1-22; Figures 3, 4, 8A, 8B, 10 and 11.	1-45, 106-129, 223, 224, 246
---		
Y		130-182, 184-195, 197-201
X	DE 2600169 A (BITZER) 14 July 1977 (14.07.1977), See English abstract.	202-205, 208, 227-230, 233
X	US 4,992,345 A (MEINTJES et al) 12 February 1991 (12.02.1991), column 2, lines 62-65; column 3, lines 5-21; column 7, lines 10-13.	214, 216, 217, 219-221, 236, 238, 239, 241-243

☒ Further documents are listed in the continuation of Box C.

See patent family annex.

## \* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;"

document member of the same patent family

Date of the actual completion of the international search

10 October 2001 (10.10.2001)

Date of mailing of the international search report

23 NOV 2001

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Commissioner of Patents and Trademarks  
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Facsimile No. (703)305-3230

Authorized officer

Susy Tsang

Telephone No. (703) 305-5900

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/23220

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:  
Please See Continuation Sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐  
☒

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/23220

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,565,082 A (NAKAMATSU et al) 15 October 1996 (15.10.1996), column 3, lines 55-67; column 4, lines 5-7.	202, 203, 209-211, 214, 217-220, 225-228, 234-236, 239-242, 245, 247
X	US 5,411,527 A (ALT) 02 May 1995 (02.05.1995), column 1, lines 25-28; column 6, lines 30-33; column 10, lines 42-68.	202, 203, 207

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/23220

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-45, drawn to a microcell assembly comprising a plurality of microcells arranged with current collectors, and the method of making the same.

Group II, claims 46-105, drawn to a microcell structure having hydrogen or oxygen permselective membrane with electrocatalyst deposited thereon, and the method of making the same.

Group III, claims 106-129, drawn to an apparatus for the manufacture of the microcell precursor article.

Group IV, claims 130-175, drawn to an electrochemical module comprising a plurality of microcells that include a plurality of hollow tubular heat exchange elements.

Group V, claims 176-201, drawn to an electrochemical device comprising water-permeable membrane hollow fibers distributed in an assembly including a plurality of microcells.

Group VI, claims 202-247, drawn to a fibrous microcell structure including an electrode that includes a current collector comprising a coated fiber.

The inventions listed as Groups I-VI do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The feature common to all of the invention is a microcell that is disclosed in US Patent No. 5,916,514. Accordingly, the inventions set forth lack a common "special technical feature" which makes a contribution over the prior art.

### Continuation of B. FIELDS SEARCHED Item 3:

EAST

search terms: fiber, fibrous, electrode, anode, cathode, current collector, graphitic, carbon, pyrolyz\$6, pyrolyz\$4, fuel cell, metal\$3, wire

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